University of Alberta

Mixed-Metal Complexes Incorporating Polydentate Bridging Ligands

by

Todd Warren Graham ©

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment
of the requirements for the degree of Doctor of Philosophy

Department of Chemistry

Edmonton, Alberta
Spring, 1999

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Faculty of Graduate Studies and Research

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To my family

Abstract

A series of hydrocarbyl-containing, dppm-bridged binuclear complexes of the form $[RhM(R)(CO)_4(dppm)_2]$ (M = Mo; R = $CO_2Me{=}CH(CO_2Me)$ (**4**), $C(CF_3){=}CH(CF_3)$ (**5**), $C(C(O)Me){=}CH_2$ (**6**), $C(CO_2Me){=}CH_2$ (**7**)) have been prepared by alkyne insertion into a metal-hydride bond. Similar species in which R = $CH{=}CH_2$, M = Mo (**8**); R = $CH{=}CH_2$, M = W(**9**); R = CH_3, M = Mo (**10**); R = η^1-$CH_2CH{=}CH_2$, M = Mo (**11**); R = $CH_2C_6H_5$, M = Mo (**12**); R = $C(O)CH_2C_6H_5$, M = Mo (**13**); R = C_6H_5, M = Mo (**14**) were obtained by halide metathesis reactions with Grignard reagents on $[RhM(\mu\text{-}Cl)(CO)_4(dppm)_2]$ (M = Mo (**2**), W (**3**)). In all hydrocarbyl species obtained, the organic fragment was bound terminally to rhodium, with four carbonyls bound to the group VI metal, two of which engage in a weak semibridging interaction with rhodium. The chloride-containing starting material, compound **2**, has been characterized crystallographically.

Protonation of the vinyl species, $[RhM(CH{=}CH_2)(CO)_4(dppm)_2]$ (M = Mo (**8**), W (**9**)) with HBF_4 at low temperature results in the formation of the alkylidene-containing species $[RhM({=}CHCH_3)(CO)_4(dppm)_2][BF_4]$ (M = Mo (**15**), W (**17**)) which rearranges to an ethylene adduct, $[RhM(\eta^2\text{-}CH_2{=}CH_2)(CO)_4(dppm)_2][BF_4]$ (M = Mo (**16**), W (**18**)) upon warming.

For the preparation of complexes containing early- and late-transition metals, the heterodifunctional ligand $M[C_5H_4CH_2CH_2PR_2]$ (M = K; R = Ph (**20**), M = Li; R = Me (**21**)) was obtained in good yield by the reaction of spiro[2.4]hepta-4,6-diene with $KPPh_2$ or $LiPMe_2$, respectively. Similar ligands, with one-carbon spacers between the Cp and PPh_2 moieties, were obtained via the reaction of fulvene or $Me_2C(C_5H_3{=}CMe_2)_2$ with diphenylphosphide, affording $K[C_5H_4CH_2PPh_2]$ (**22**) and $(Li)_2[Me_2C(C_5H_3CMe_2PPh_2)_2]$

(24), respectively. The metallocene-dichloride derivatives of these ligands were obtained via halide displacement from $TiCl_3(THF)_3$, $TiCl_4(THF)_2$, $ZrCl_4$, or $ZrCl_4(THF)_2$ to give $[(\eta^5\text{-}C_5H_4(CH_2)_nPPh_2)_2MCl_2]$ (M = Ti and n = 2 (**25**), n = 1 (**27**); M = Zr and n = 2 (**26**), n = 1 (**28**)) and the ansa-derivative $[Me_2C(C_5H_3CMe_2PPh_2)_2ZrCl_2]$ (**29**). Compound **26** has been characterized crystallographically.

Reaction of compounds **25** and **26** with $(COD)Mo(CO)_4$ provides the binuclear species, $[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)_2MCl_2Mo(CO)_4]$ (M = Ti (**30**), Zr (**31**)), both of which were characterized by X-ray diffraction. Reaction of **25** or **26** with $[RhCl(CO)_2]_2$ at low temperature under high dilution conditions yields α- and β-$[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4\text{-}CH_2CH_2PPh_2)_2MCl_2RhCl(CO)]_2$ (M = Ti (**32a** and **b**), Zr (**33a** and **b**). Compound **32** has been characterized crystallographically, which showed the compound possesses a macrocyclic, tetranuclear structure. Compounds **32a** and **33a** were obtained pure, and were found to slowly isomerize to the new species, **32b** and **33b**, respectively over a period of several days.

Reaction of $[(\eta^5\text{-}C_5H_4CH_2PPh_2)_2MCl_2]$ (M = Ti (**27**), Zr (**28**)) with $[RhCl(CO)_2]_2$ produces the tetranuclear complexes $[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4CH_2PPh_2)_2MCl_2RhCl(CO)_2]_2$ (M = Ti (**34**), Zr (**35**)), and compound **34** was characterized by X-ray diffraction. $[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4CH_2PPh_2)_2TiCl_2PdCl_2]_2$ (**36**) was prepared similarly and was shown to contain four metals by a molecular weight determination.

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List of Abbreviations and Symbols

anal.	analysis
ca.	circa (approximately)
calcd.	calculated
Cp	cyclopentadienyl
DMAD	dimethylacetylenedicarboxylate
dmpm	bis(dimethylphosphino)methane
dppm	bis(diphenylphosphino)methane
h	hour(s)
HFB	hexafluoro-2-butyne
IR	infrared
Me	methyl
MeOH	methanol
mg	milligrams
min	minute(s)
mL	millilitres
mmol	millimoles
MHz	megahertz
NMR	nuclear magnetic resonance
^{i}Pr	isopropyl
Ph	phenyl, C_6H_5-
THF	tetrahydrofuran
^{t}Bu	tertiary butyl
µL	microlitres

Crystallographic Abbreviations and Symbols

a, b, c	unit cell lengths
deg (or °)	degrees
F_c	calculated structure factor
F_o	observed structure factor
$GOF(S)$	goodness of fit
h, k, l	Miller indices defining lattice planes, where the plane intersects the unit cell axes at 1/h, 1/k 1/l of the respective lengths a, b, and c.
R_1	residual index (a measure of agreement between calculated and observed structure factors)
wR_2	weighted residual index
V	unit cell volume
w	weighting factor applied to structure factor
Z	number of molecules per unit cell
Å	Ångstrom(s) (1Å = 10^{-10} metres)
α, β, γ	angles between *b* and *c*, *a* and *c*, and *a* and *b* axes, respectively, of unit cell
λ	wavelength
ρ	density
σ	standard deviation

Chapter 1

Introduction

One of the major goals of research in catalysis is the design of catalysts that can more efficiently effect the transformation of inexpensive and readily available feedstocks, such as carbon dioxide and carbon monoxide, into useful, valuable products. Generally, catalysts that are used industrially to effect these transformations are heterogeneous, because of their ease of preparation and separation from reaction products, and because of their typically robust nature.[1] In spite of these advantages, obtaining information about substrate reactivity on a molecular level has been difficult, so that little is understood about these heterogeneous processes. The development of heterogeneous catalysts has thus been very much empirical, as rational design is not possible without mechanistic information. Moreover, the specificity of heterogeneous catalysts is often poor, owing to the many different reactive sites available on a heterogeneous surface.[2]

Mechanistic information in heterogenous systems can often be inferred from results obtained in related homogeneous systems.[3] These are much more amenable to study, due to the availability of a wide range of spectroscopic techniques, and are often used as models for the transformations that occur in a heterogeneous reaction. Accordingly, the study of soluble systems may provide useful information about important intermediates in a heterogeneous catalytic sequence, leading to a more detailed understanding of individual catalytic steps. This information may be utilized to optimize the specificity of a catalytic reaction, leading to more efficient usage of raw materials.

Homogeneous systems are not only useful as model systems, they can act as catalysts in their own right.[4] Owing to the tremendous variety of ligands available, the electronic and steric environment of the attached metals may be tuned to obtain highly specific catalysts and excellent results have been obtained in several important applications. For example, the production of an important L-Dopa precursor is achieved industrially with a highly stereoselective chiral rhodium catalyst.[5] Another important example of homogeneous catalysis is the Sharpless epoxidation, in which chiral epoxides are produced catalytically from prochiral olefins, using $Ti(O^iPr)_4$/diethyl tartrate/t-BuOOH in carefully controlled ratios.[6]

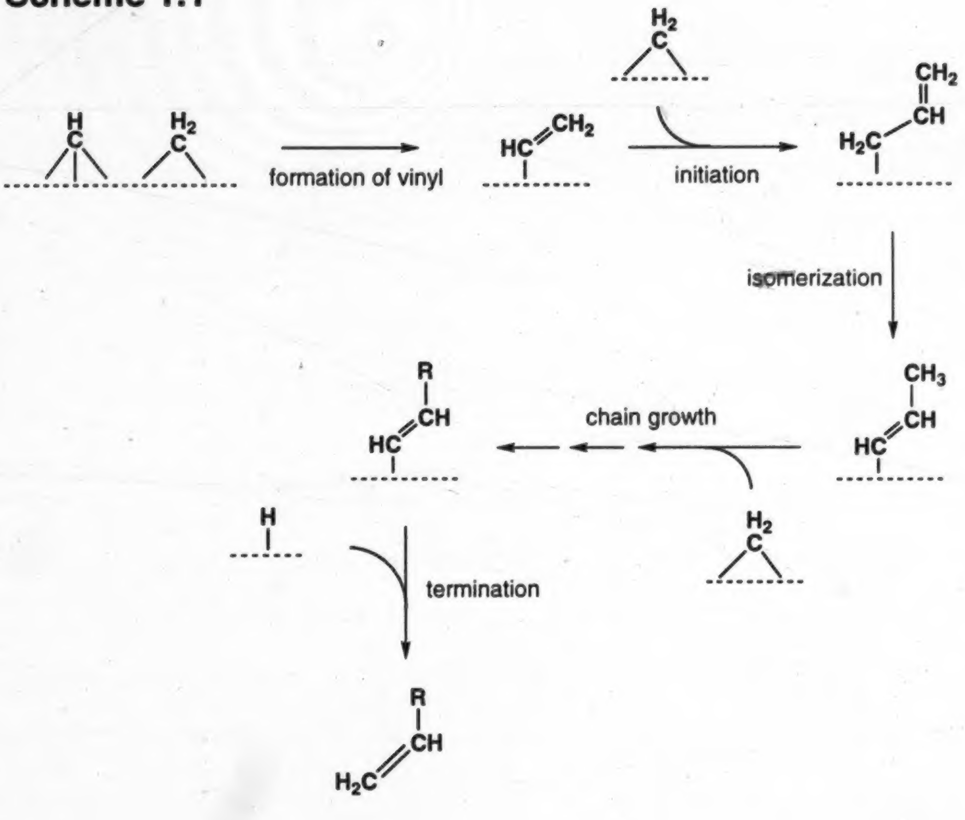
Mononuclear complexes are often used to model reactions that are thought to occur at a metal surface. These studies have resulted in a wealth of information about a variety of reaction types, including oxidative addition,[7] reductive elimination,[8] and migratory-insertion reactions.[9] Direct comparison of the reactivity of a mononuclear complex with that of a heterogeneous catalyst can be problematic though, owing to the presence of many adjacent metals on a metal surface in the heterogeneous system, in which metal-metal interactions may significantly alter the course of a reaction.[10]

The study of cluster complexes, containing many metal atoms connected by metal-metal bonds or bridging ligands, may provide a more realistic approximation to a metal surface because of the many metal sites available for interaction with substrate molecules. In fact, a cluster-surface analogy has been suggested by Muetterties, in which a cluster complex may be viewed as a small piece of metal with many chemisorbed species on the periphery, and has provided a significant driving force for the study of polynuclear transition metal complexes.[11]

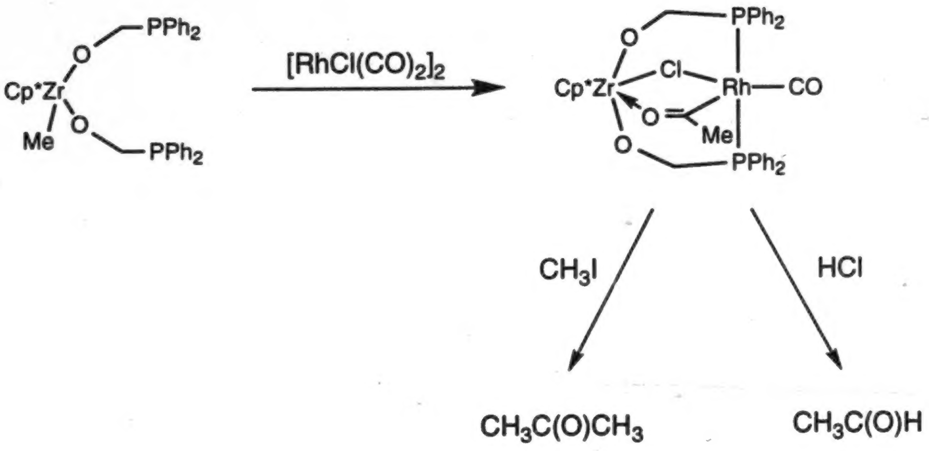
The Fischer-Tropsch (FT) reaction is an important heterogeneously-catalyzed reaction because it produces a variety of useful hydrocarbon products from the inexpensive feedstocks, CO and H_2.[12] A variety of metals may be used as catalysts with, as one might expect, differing selectivities for the different catalysts.[12b] A recent mechanistic proposal for this reaction has been put forth by Maitlis, in which surface-bound vinyl groups are formed by the condensation of metal-bound "CH" and "CH_2" fragments, which may then migrate to a CH_2 fragment to lengthen the chain. A key step in the proposal is the isomerization of the η^1-allyl group to form a substituted vinyl moiety, which can subsequently migrate to another surface-bound methylene, resulting in overall chain growth, as diagrammed below in Scheme 1.1.[12a] This proposal was suggested on the basis of model studies carried out on binuclear metal complexes[12c-f] and has received support from isotopic labelling studies in the heterogeneous systems.[12g-k] Thus, model organometallic complexes containing hydrocarbyl fragments are of interest in order to study the feasibility of the proposed reaction steps. No matter which of the proposed FT mechanisms are considered, the pivotal fragment is invariably a methylene group which, in the heterogeneous system, is proposed to bridge two metals. C-C chain growth involves insertion of different hydrocarbyl fragments into a metal-methylene bond,[13] and a number of methylene-bridged complexes have demonstrated reactivity that closely models such sequences.[12d, 14]

Lately, there has been much emphasis on catalysts containing different metals, due to the novel reactivities that may result from the combination of metal types. For example, BP Chemicals Limited has recently developed a mixed-metal Ir/Ru-containing catalyst which converts MeOH and CO to acetic acid.[15] In addition, ethylene glycol formation from synthesis gas has been found to be promoted by a mixed Rh/Ru catalyst, and although homonuclear systems containing either of these metals are known to produce C_2 oxygenates, the selectivity has been found to be much improved in the heteronuclear system.[16] Other types of mixed-metal catalysts are those containing the Co/Mo[17] and Pt/Re[17] metal combinations which are used for hydrodesulfurization and gasoline reforming, respectively, and the Rh/Pt combination which is commonly used in catalytic converters for the scrubbing of exhaust from automobiles.

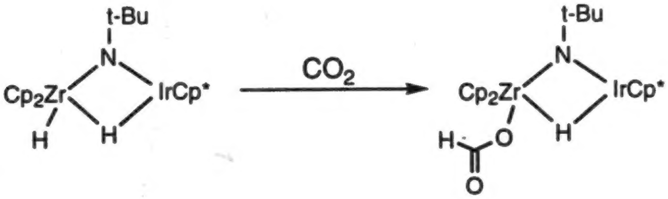
Scheme 1.1


H
C
H2
C
formation of vinyl
HC
CH2
H2
C
initiation
CH2
CH
H2C
isomerization
CH3
CH
HC
chain growth
H2
C
R
CH
HC
H
termination
R
CH
H2C

In heteronuclear systems, the metals may have subtle differences, as in systems containing two different late metals,[18] or they may be widely divergent as in those containing both early- and late-transition metals. The latter type of system has generated much interest recently,[19] due to observations that group 8, 9 or 10 metals supported on titanium oxides exhibit enhanced reactivity towards the hydrogenation of CO_2, producing methanol and formates, compared to when these metals were supported on alumina or silica.[20] This increase in reactivity has been attributed to metal-metal cooperativity between the early- and late-metals and is often referred to as the "strong metal-support interaction."[20] Placing two such metals with very different electronic properties in a proximate arrangement should result in a significantly polar environment, which may lead to novel and interesting reactivity patterns. In fact, calculations have shown that in metal-metal bonded systems, the bond between the early and late metals should have significant donor-acceptor character.[21e] Many soluble model systems containing these metal types have been prepared, with varying degrees of success in the activation of substrates such as CO or CO_2.[21] The example below shows how metal-metal cooperativity effects between early and late metals can aid in the formation of oxygenates from carbon monoxide, with μ-η^1:η^1-acyl ligand formation promoted by the oxophilic early metal.[21] The formation of a bridging acetyl group, and coordination of π-acids as well as an oxidative-addition reaction occurs at the late metal.[21e] Clearly, the study of multinuclear complexes containing such disparate metals could provide insights into the source of these differing reactivities towards the hydrogenation of carbon oxides, and may lead to the production of useful catalysts to effect these transformations.


PPh2
Cp*Zr
Me
PPh2
[RhCl(CO)2]2
Cp*Zr
Cl
Rh
CO
Me
PPh2
PPh2
CH3I
HCl
CH3C(O)CH3
CH3C(O)H

A variety of early-late heterobinuclear (ELHB) complexes have been prepared which are capable of CO_2 activation,[21a-c] but reports on the subsequent derivatization of activated CO_2 are scarce.[19d, 21c] Recently though, Bergman has reported a Zr/Ir containing complex which may be used to achieve the stoichiometric reduction of CO_2 to formate, as shown below.[21c]

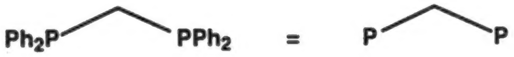

t-Bu
N
Cp2Zr
IrCp*
H
H
CO2
t-Bu
N
Cp2Zr
IrCp*
H
O
H
O

These results are promising in that they show the utility of early-late metal-metal cooperation in the activation of a polar substrate.

The simplest polynuclear species in which cooperativity effects can be studied is one that contains two metals, and these binuclear systems are of interest for a number of reasons. They tend to be soluble and as such may be characterized by standard spectroscopic techniques, and the presence of two metals allows for metal-metal cooperativity but avoids the difficulties often encountered in characterizing higher nuclearity clusters, due to the presence of fewer ligands.

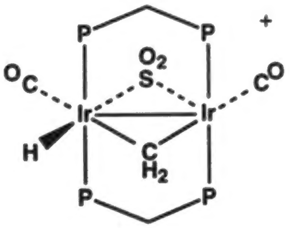
Since binuclear complexes with unsupported metal-metal bonds suffer from a tendency to dissociate,[22] it is desirable to maintain the proximity of the two metal centers through the use of a multidentate bridging ligand, which serves to prevent the fragmentation of the complex to mononuclear species.

Bis(diphenylphosphino)methane (dppm) is commonly used to achieve this goal as it appears to have the ideal bite angle for the formation of binuclear complexes, in that it tends to bridge two metals rather than chelate, and yet is flexible enough to allow for the reversible formation of metal-metal bonds.[23] These characteristics have been exploited for the preparation of a wide variety of dppm-bridged binuclear complexes.[24] In addition, the presence of 100 % abundant, NMR-active ^{31}P nuclei greatly aids in the characterization of the complexes. ^{1}H NMR spectroscopy also provides useful structural information, due to the presence of the two methylene hydrogens in the PCH_2P framework.

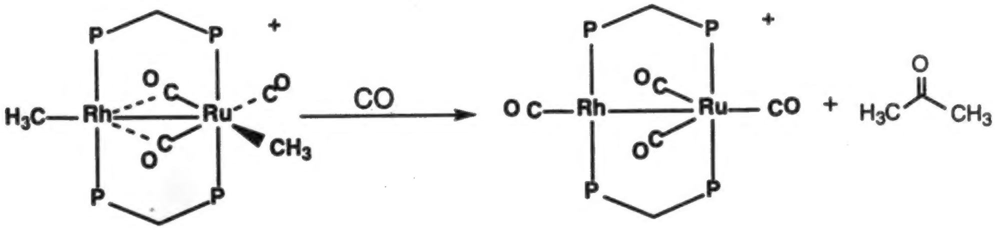


dppm

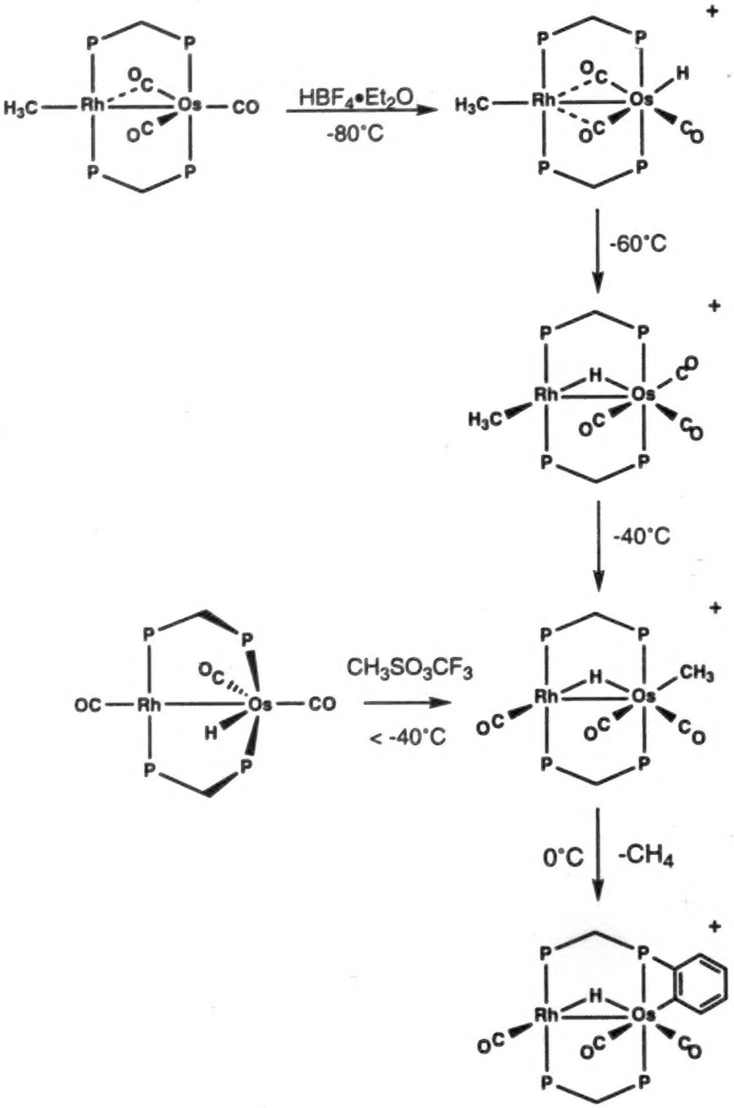
Previous work in our group on dppm-bridged binuclear systems shows that adjacent metals can assist in ligand activation.[25] For example, it has been found that exchange between the hydride and bridging methylene groups is very facile in the diiridium species shown below, with an activation energy of only 6 kcal/mol.[25d] Recent work on alkyl groups bound to a platinum surface has shown that activation energy barriers for the interconversion between methyl and methylene fragments are on the order of 6-8 kcal/mol.[26] The similarity of these values for the homogeneous and heterogeneous systems offers further support that binuclear complexes can function as useful models for metal surfaces and that metal-metal cooperativity effects can be of comparable magnitude in such systems.



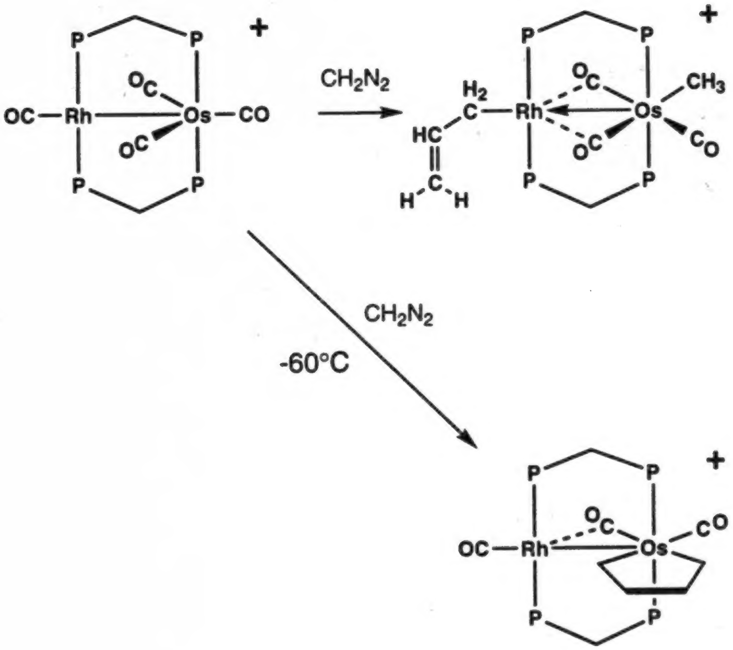
Many other binuclear dppm-bridged systems have been studied in our group, containing the Rh/Ir,[25b, c], Rh/Re,[24a] and Rh/Mn[24a, 27] metals, as well as Rh/Os[18a, 29] and Rh/Ru[24, 29] metal combinations. The latter two systems have shown a rich and varied chemistry with hydrocarbyl ligands,[28-29] which is of particular relevance to a metal surface. The site specific reductive elimination of methane, summarized in Scheme 1.2, demonstrates the mobility of ligands over a bimetallic core, and the preference for reductive elimination to occur from one metal over the other.[18a] The formation of either an allyl-methyl species or the osmacyclopentane complex under subtly different conditions, shown in Scheme 1.3 below, has provided a model for methylene chain growth on a metal surface.[28] In a related Rh/Ru system, reductive elimination of acetone from the dimethyl species, shown below, occurs under a carbon monoxide atmosphere. Although the mechanism is not currently known, it has been suggested that acyl formation occurs at Ru, followed by subsequent methyl migration from rhodium to ruthenium and then



Scheme 1.2

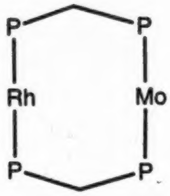

H₃C
Rh
Os
CO
P
HBF₄•Et₂O
-80°C
H
+
-60°C
-40°C
CH₃SO₃CF₃
< -40°C
CH₃
OC
0°C
-CH₄

Scheme 1.3


CH$_2$N$_2$
CH$_2$N$_2$
-60°C
OC—Rh
Os—CO
CH$_3$
P
+

reductive elimination of the organic fragments.[29]

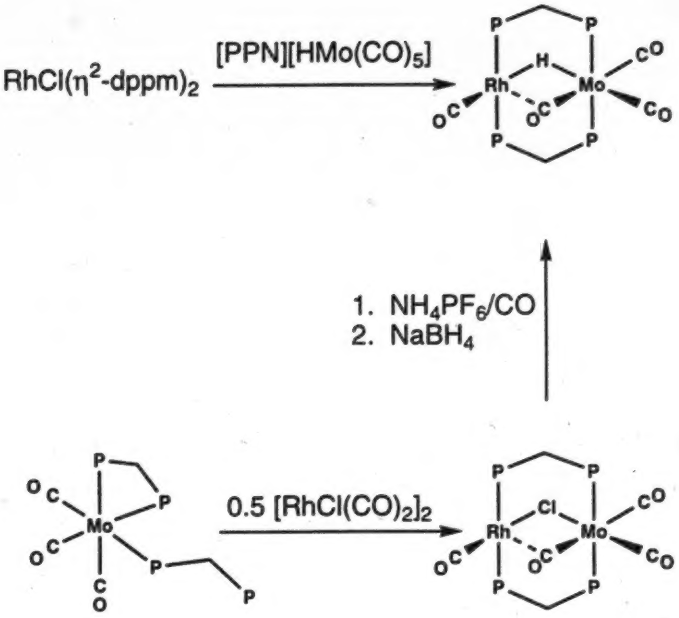
In view of this fascinating chemistry, we were interested in extending the heterobinuclear chemistry to the left in the Periodic Table. In particular, we felt that an the examination of the reactivity of hydrocarbyl fragments bound to a Rh/Mo core in the framework shown below would provide useful contrasts with the Rh/group VIII combinations, in terms of the differing effects of placing Mo *vs.* Os or Ru proximate to a Rh center.



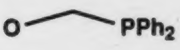
Previous preliminary work on this system has been carried out by Shaw,[24b, 30] and by our group.[24a] The chloride species, $[RhMo(CO)_4(\mu\text{-}Cl)(dppm)_2]$, which proved to be an important precursor complex in this work, has been prepared by Shaw,[24b] and may be readily converted to the hydride-containing species $[RhMo(CO)_4(\mu\text{-}H)(dppm)_2]$.[31] Dppm-bridged Rh/group VI complexes may also be prepared, as has been reported in our group, directly from mononuclear complexes.[24a] These reactions are diagrammed in Scheme 1.4.

We were also interested in investigating heterobinuclear systems in which the electronic differences between the two metals was even greater than for the above Rh/Mo system, so we turned to systems which contain a late-transition metal and an early metal, such as those from group IV (Ti, Zr, and Hf). In this case dppm is no longer an appropriate choice for a bridging ligand, due to the expected labile nature of a phosphine ligand on a typically high-oxidation state, early transition metal. The ligand chosen should be capable of forming strong bonds to both early and late transition metals, and a

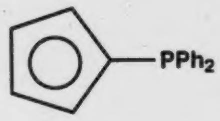
Scheme 1.4


RhCl(η²-dppm)₂
[PPN][HMo(CO)₅]
1. NH₄PF₆/CO
2. NaBH₄
0.5 [RhCl(CO)₂]₂
P
Rh
Mo
H
Cl
CO
OC

number of ligands have been reported which fulfill these criteria, examples of which are shown below.[31]



A

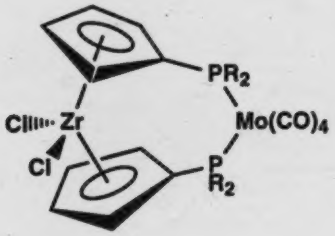


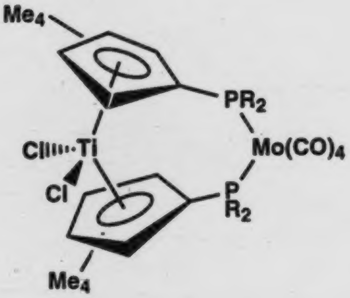
B

The ligand shown in **A** has provided excellent results for the Wolczanski group,[21e, 30a, b] in the preparation and subsequent reactivity studies of early-late heterobimetallic (ELHB) complexes. However, since Cp ligands are exceedingly common in early-metal chemistry, we felt that it was desirable to incorporate this functionality into a bridging group of the type shown in **B**,[32d-g] thus maximizing the number of potential substrate binding sites on the early-metal bis-Cp species. Our strategy for the preparation of ELHB complexes was to first bind the Cp part of a ligand like that shown in **B** to an early metal, and then use these metallocene dichloride species as metalloligands for late transition metals.

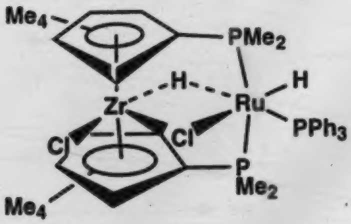
A number of ELHB complexes have been reported with the Cp-phosphine ligand shown above in **B**. The literature has shown that in the bis-cyclopentadienyl-type systems, the ligand is too restricted to allow for facile group transfer between metal centers,[32e, h] which was an important goal of this study, as we were interested in placing hydrocarbyl groups on both metal types to study reactions such as migratory insertions and reductive eliminations. This is easily explained by considering the geometric features of the ligand when bound to an early transition metal. Since a typical Cp(centroid)-Cp(centroid) distance on a group IV metallocene dichloride is 3.8 to 4.2 Å,[33] and the P-P separation in a late metal, bis-phosphine complex having a trans phosphine arrangement is usually around 4.4 Å,[34] the required tilting of the cyclopentadienyl rings in a Cp_2MX_2-

type system, will force the early-metal substituents away from the late metal, as is shown below. This has been found in several systems in which the products were crystallographically characterized.[32e, g] Note also, that in these complexes the phosphines are bound mutually cis to the molybdenum center, resulting in large metal-metal separations.

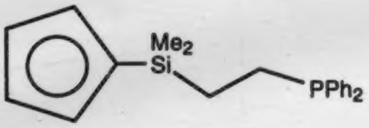


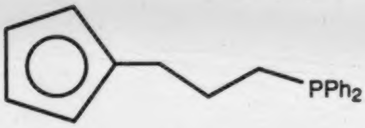


There has been one reported case, as depicted below, in which the phosphines on a late metal are bound approximately trans, and an early-metal derived halide is bridging the two metals, but the system appears to be quite strained, based on the Me_2P-Ru-PMe_2 bond angle of about 157°.[32d] As in the dppm system, we wanted a bridging ligand that was flexible enough for the reversible formation of metal-metal bonds and ligand migration between metal centers,[18a] which are certainly important considerations in metal-metal cooperativity. We felt that the perceived lack of flexibility in the directly bonded Cp-PR_2 systems could be alleviated by the introduction of an alkyl spacer between the Cp and PR_2 moieties.

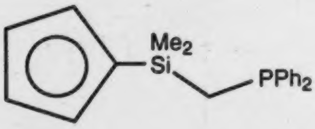


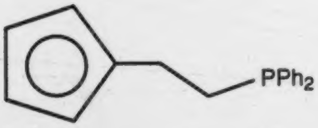
Ligands of this type have been reported in the literature, containing varying numbers of spacer atoms between the Cp and PR_2 units. Several with a three atom spacer, such as those shown below have been reported,[35] however we felt that this type of bridging ligand would result in too large of a metal-metal separation for effective metal-metal cooperativity.



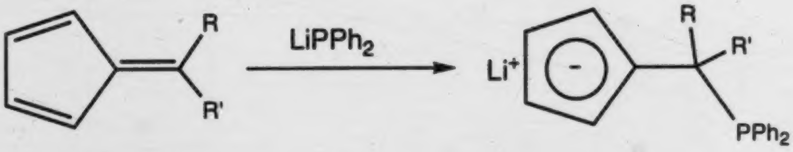


Ligands with a two-atom spacer have also been reported by several groups,[36] some examples of which are shown below.





Recently, while this work was nearing completion, Erker reported the preparation of several ligands with a one-atom spacer (see below),[37] and the subsequent reactivity of substituted metallocene dichlorides containing these ligands with a variety of late-metal sources.[38]



As we were interested in extending our studies of heterobinuclear complexes from those containing mid- or late-metal/late metal combinations, bridged by bis-diphenylphosphinomethane, to systems containing early- and late-transition metals, we decided to investigate the reactivity of metallocene dichlorides containing pendant alkylphosphino groups bound to the cyclopentadienyl rings with late-metal sources.

This thesis describes the preparation and reactivity of a variety of binuclear dppm-bridged hydrocarbyl complexes containing the Rh/Mo combination of metals. In addition, the preparation and characterization of a variety of heteronuclear complexes containing both group IV and late metals, bridged by cyclopentadienylalkylphosphines is described, an important aspect of which is the effect of spacer length on the structure of the products obtained.

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Chapter 2

Hydrocarbyl Complexes of Rhodium and Molybdenum Bridged by Bis(diphenylphosphino)methane

Introduction

Currently there is considerable industrial interest in the development of catalysts containing two or more different metals, applications for which can be found in a number of processes, including coal hydrodesulfurization, methanol carbonylation, naptha reforming and olefin oxidation.[1] In addition, the use of Rh/Pt mixed-metal catalysts is widespread in the scrubbing of exhaust gases from automobile engines.[1] Most of these are heterogeneous processes, and in spite of their economic importance, little is understood about the role of the different metals due to the inherent difficulty in studying reactions that occur under these conditions. One approach used to obtain information about heterogeneous systems is to use appropriate homogeneous systems as models, from which information about key steps in the catalytic transformation can be obtained.

Square-planar Rh(I) and Ir(I) complexes have played an important role in the elucidation of many of these key steps in a variety of homogeneous catalytic reactions, and much of what has been learned from these studies can be applied to heterogeneous processes.[2a-c] In catalytic processes involving organic transformations, metal alkyls are often important intermediates. Consequently, studies of stable alkyl or related complexes can yield valuable information about their reactivities. Although the alkyl chemistry of many mononuclear systems has been studied extensively,[2d-g] these systems are not ideal models of heterogeneous processes owing to the presence of only one metal in the mononuclear complexes, compared to the availability of many adjacent sites in the heterogeneous system. Consequently, the study of alkyl complexes containing two or more metals can provide important insights into cooperativity effects that may occur in multinuclear systems. A variety of binuclear alkyl and alkenyl Rh(I)-containing complexes have been prepared,[3-6] but little is understood about the role of the adjacent metal in the reactivity of the organic fragments. Thus, the study of stable binuclear Rh(I)-containing alkyl complexes can provide important information on how the adjacent metal affects the reactivity of an alkyl fragment.

Bimetallic hydrocarbyl complexes bridged by dppm and containing the Rh/Ir,[3a] Rh/Os,[4a, b] Rh/Ru,[5] Rh/Re[6] and Rh/Mn[7] combinations have been prepared previously in our group. We were interested in extending this chemistry to complexes containing rhodium together with a group VI metal in order to investigate the effect of the adjacent metal on the reactivity of the alkyl moiety. In particular, we were interested in the nature of the metal-alkyl interactions and the effect of a proximate metal on the reactivity of the alkyl fragment in a variety of reaction types, including migratory insertion and also the possibility of reductive eliminations from bimetallic dialkyl or alkyl-hydrido species. The ultimate goal is to develop a better understanding of the metal-metal cooperativity effects that are possible in these systems.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of prepurified argon. Solvents were dried and distilled under nitrogen immediately before use. Sodium benzophenone was used as the drying agent except with CH_2Cl_2 which was distilled from P_2O_5. Hydrated rhodium trichloride was purchased from Johnston Matthey Ltd, whereas the group VI metal hexacarbonyls were purchased from Aldrich and were used as received. Bis(diphenylphosphino)methane (dppm), $HBF_4{\bullet}(OMe_2)_2$, all Grignard reagents and alkynes were purchased from Aldrich and were used as received.

99% ^{13}CO was purchased from Isotec Inc. The compounds $[M(CO)_3(dppm)_2]$ (M = Mo,[8] W[9]), $[RhCl(CO)_2]_2$,[10] and $[RhMo(CO)_4(\mu\text{-}H)(dppm)_2]$ **(1)**,[11] and $[RhMo(CO)_4(\mu\text{-}Cl)(dppm)_2]$ **(2)**,[12a, b] $[RhW(CO)_4(\mu\text{-}Cl)(dppm)_2]$ **(3)**[12a] were prepared according to published procedures.

All ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker AM-400 spectrometer operating at 400.1, 162.0 and 100.6 MHz for the respective nuclei. The internal deuterated solvent served as a lock for the spectrometer. All infrared spectra were run on a Nicolet 7199 FT interferometer as solids in Nujol or dichloromethane casts on KBr. The elemental analyses were performed by the microanalytical service within the department. Spectroscopic data for all compounds are given in Table 2.1.

Preparation of Compounds. (a) $[RhMo(MeO_2CC{=}C(H)CO_2Me)(CO)_4\text{-}(dppm)_2]$ (4). 20 µL (0.163 mmol) of $CH_3O_2CC{\equiv}CCO_2CH_3$ (DMAD) was added to 100 mg (0.0925 mmol) of compound **1** in 10 mL of THF. The mixture was stirred for 1 h then 20 mL of n-pentane was added, resulting in the precipitation of an orange solid. The solvent was removed via cannula and the solid washed with 3×10 mL of n-pentane. Yield 92 mg, 81%. Anal. Calcd. for $C_{60}H_{51}P_4O_8RhMo$: C, 58.94%; H, 4.20%. Found, C, 59.01%; H, 4.23%.

(b) $[RhMo(C(CF_3){=}C(H)CF_3)(CO)_4(dppm)_2]$ (5). Hexafluoro-2-butyne (HFB) was bubbled slowly for one min through a solution of 54 mg (0.0500 mmol) of **1** in 10 mL of THF, resulting in a color change from dark red to light orange. The mixture was stirred for 20 min then the solvent removed in vacuo. The yellow residue was recrystallized from CH_2Cl_2/Et_2O. Yield 56 mg, 89%. Anal. Calcd. for $C_{58}H_{45}F_6P_4O_8RhMo$: C, 56.06%; H, 3.65%. Found: C, 56.40%; H, 3.63%.

(c) $[RhMo(H_2C{=}CC(O)Me)(CO)_4(dppm)_2]$ (6). 14 µL (0.179 mmol) of 3-butyn-2-one was added to a solution of 100 mg (0.0925 mmol) of compound **1** in 10 mL

Table 2.1 Spectroscopic Data for Compounds[a]

		NMR[c]	
compound:	IR(cm-1)[b]	$\delta(^{31}P\{^1H\})$ (ppm)	$\delta(^1H)$ (ppm)[f]
$RhMo(MeO_2CC{=}C(H)CO_2Me)$-$(CO)_4(dppm)_2$ (**4**)	1978(vs) 1908(s) 1813(vs) 1760(s) 1700(s)	23.9(dm, $^1J_{Rh\text{-}P}$ = 136.1 Hz, Rh-*P*), 38.9(m, Mo-*P*)	2.91(m, 4H, $Ph_2PCH_2PPh_2$), 3.05(s, 6H, CO_2CH_3), 4.56(d, 1H, $^3J_{Rh\text{-}H}$ = 2.5Hz, $MeO_2C(H)C{=}CCO_2Me(Rh)$)
$RhMo(F_3CC{=}C(H)CF_3)(CO)_4$-$(dppm)_2$ (**5**)	1978(vs) 1923(vs) 1788(m)	22.0(dm, $^1J_{Rh\text{-}P}$ = 132.8 Hz, Rh-*P*) 38.7(m, Mo-*P*)	2.98(m, 4H, $Ph_2PCH_2PPh_2$) 5.15(m, 1H, $^3J_{HF}$ = 10.0 Hz, $CF_3(H)C{=}CCF_3(Rh)$)
$RhMo(H_2C{=}CCOMe)(CO)_4$-$(dppm)_2$ (**6**)[d]	1965(vs) 1911(vs) 1776(s) 1739(s) 1646(m)	23.2(dm, $^1J_{Rh\text{-}P}$=144.0 Hz, Rh-*P*) 41.0(m, Mo-*P*)	1.15(s, 3H, $H_2C{=}CCOMe$) 2.95(m, 4H, $Ph_2PCH_2PPh_2$) 5.36(bs, 1H, $H_2C{=}CCOMe$, cis to Rh) 5.59(d, 1H, $^3J_{Rh\text{-}H}$=4.3 Hz, $H_2C{=}CCOMe$, trans to Rh)
$RhMo(H_2C{=}CCO_2Me)(CO)_4$-$(dppm)_2$ (**7**)	1975(vs) 1921(vs) 1771(vs) 1738(s) 1698(m)	22.5(dm, $^1J_{Rh\text{-}P}$ =141.1 Hz, Rh-*P*) 40.9(m, Mo-*P*)	2.75(s, 3H, $H_2C{=}CCO_2Me$) 2.95(m, 4H, $Ph_2PCH_2PPh_2$) 5.05(bs, 1H, $H_2C{=}CCO_2Me$, cis to Rh) 5.91(m, 1H, $^3J_{Rh\text{-}H}$ = 4.0 Hz, $^1J_{HH}$ = 1.8 Hz, $H_2C{=}CCO_2Me$, trans to Rh)

Table 2.1 (cont.)

RhMo(CH=CH$_2$)(CO)$_4$-(dppm)$_2$^{d}(8)	1968(vs) 1919(m) 1776(s) 1760(s)	25.35(dm, $^1J_{Rh\text{-}P}$ = 149.3Hz, Rh-*P*) 43.20(m, Mo-*P*)	2.60(m, 4H, Ph$_2$PC*H*$_2$PPh$_2$) 4.27(dm, ^{1}H, $^3J_{HH}$ = 18 Hz, CH=C*H*$_2$) 5.09(dm, 1H, $^3J_{HH}$ = 11Hz, CH=C*H*$_2$) 6.75(m, 1H, C*H*=C*H*$_2$)
RhW(CH=CH$_2$)(CO)$_4$-(dppm)$_2$^{d}(9)	1967(vs) 1903(m) 1771(s) 1749(s)	27.5(dm, $^1J_{Rh\text{-}P}$ = 149.4Hz, Rh-*P*) 18.3 (m, W-*P*)	2.95(m, 4H, Ph$_2$PC*H*$_2$PPh$_2$) 4.25(dm, ^{1}H, CH=C*H*$_2$) 5.15(dm, 1H, CH=C*H*$_2$) 6.78(m, 1H, C*H*=CH$_2$
RhMo(CH$_3$)(CO)$_4$(dppm)$_2$^{d} (10)	1952(vs) 1900(vs) 1762(vs) 1744(vs)	31.72(dm, $^1J_{Rh\text{-}P}$ = 147.7Hz, Rh-*P*) 43.23(m, Mo-*P*)	0.15(dt, 3H, $^2J_{Rh\text{-}H}$ = 2.3Hz, $^3J_{H\text{-}P}$ = 7.5Hz, Rh-C*H*$_3$) 2.85(m, 4H, Ph$_2$PC*H*$_2$PPh$_2$)
RhMo(η^1-CH$_2$CH=CH$_2$)(CO)$_4$-(dppm)$_2$^{d,e}(11)	1963(vs) 1907 (s) 1760(s)	28.27(dm, $^1J_{Rh\text{-}P}$ = 152.9Hz, Rh-*P*) 41.89(m, Mo-*P*)	2.74(m, 2H, C*H*$_2$CH=CH$_2$) 2.85(m, 4H, Ph$_2$PC*H*$_2$PPh$_2$) 3.46(m, 1H, CH$_2$CH=CH*H*$_{trans}$) 4.10(dm, 1H, CH$_2$CH=CH*H*$_{cis}$) 5.87(m, 1H, CH$_2$C*H*=CH$_2$)
RhMo(CH$_2$Ph)(CO)$_4$(dppm)$_2$^{d} (12)	1954(vs) 1890(s)	26.12(dm, $^1J_{Rh\text{-}P}$=151.4Hz, Rh-*P*)	2.66(dt, 2H, $^2J_{Rh\text{-}H}$ = 3.5 Hz, $^3J_{P\text{-}H}$ = 7.5Hz,

Table 2.1 (cont.)

	1788(s)	41.45(m, Mo-*P*)	Rh-C*H*$_2$Ph) 2.93(m, 4H, Ph$_2$PC*H*$_2$PPh$_2$) 5.63(m, 2H C$_6$*H*$_5$CH$_2$) 6.35(m, 3H, C$_6$*H*$_5$CH$_2$)
RhMo(C(O)CH$_2$Ph)(CO)$_4$-(dppm)$_2$[d,g] (13)	1600(m)	17.3(dm, $^1J_{Rh-P}$=167.9Hz, Rh-*P*) 40.9(m, Mo-*P*)	2.95(m, 4H, Ph$_2$PC*H*$_2$PPh$_2$) 3.15(s, 2H, RhC(O)C*H*$_2$Ph)
RhMo(Ph)(CO)$_4$(dppm)$_2$[d] (14)	1953(vs) 1907(s) 1763(vs)	23.65(dm, $^1J_{Rh-P}$ = 148.7Hz, Rh-*P*) 41.74(m, Mo-*P*)	2.96(m, 4H Ph$_2$PC*H*$_2$PPh$_2$) 5.97(m) 2H, C$_6$*H*$_5$[d]) 6.09(m, 1H, C$_6$*H*$_5$[d]) 6.50(m, 2H, C$_6$*H*$_5$[d])
[RhMo(=CHCH$_3$)(CO)$_4$-(dppm)$_2$][BF$_4$][h] (15)		11.7(dm, $^1J_{Rh-P}$=146.1, Rh-*P*) 39.4(m, Mo-*P*)	1.73(d, 3H, $^3J_{HH}$ = 7.3 Hz =CHC*H*$_3$) 3.01(m, 4H, Ph$_2$PC*H*$_2$PPh$_2$) 18.81(m, 1H, $^3J_{HH}$ = 7.3 Hz, =C*H*CH$_3$)
[RhMo(η^2-H$_2$C=CH$_2$)(CO)$_4$-(dppm)$_2$][BF$_4$] (16)	2010(vs) 1967(m) 1832(s) 1813(s)	29.9(dm, $^1J_{RhP}$=131.2 Hz, Rh-*P*) 37.3(m, Mo-*P*)	3.10(m, 4H Ph$_2$PC*H*$_2$PPh$_2$) 3.58(s, 4H, C$_2$*H*$_4$)
[RhW(=CHCH$_3$)(CO)$_4$-(dppm)$_2$][BF$_4$][h] (17)		26.9(dm, $^1J_{RhP}$=147.2 Hz, Rh-*P*) 17.0(m, Mo-*P*)	1.71(d, 3H, $^3J_{HH}$ = 7.5 Hz, =CHC*H*$_3$) 3.2(m, 4H, Ph$_2$PC*H*$_2$PPh$_2$) 18.79(m, 1H, $^3J_{HH}$ = 7.5 Hz, =C*H*CH$_3$)

Table 2.1 (cont.)

[RhW(η^2-$H_2C{=}CH_2$)(CO)$_4$-(dppm)$_2$][BF_4] **(18)**		31.7(dm, $^1J_{Rh\text{-}P}$=110 Hz, Rh-*P*) 13.1(m, Mo-*P*)	3.30(m, 4H, $Ph_2PCH_2PPh_2$) 3.59(s, 4H, C_2H_4)
[RhMo(PhC_2H)(CO)$_4$(dppm)$_2$]-[BF_4] **(19)**	2007(s) 1979(vs) 1843(m)	26.4(dm, $^1H_{Rh\text{-}P}$ = 103 Hz, Rh-*P*) 34.7(m, Mo-*P*)	2.59(m, 2H, $Ph_2PCH_2PPh_2$) 3.25(m, 2H, $Ph_2PCH_2PPh_2$) 6.58(m, 3H, PhC_2H) 7.09(m, 2H, PhC_2H)

[a] Abbreviations used: for IR spectra, (vs) very strong; (s) strong; (m) medium; for NMR (dt) doublet of triplets, (m) multiplet, (dm) doublet of multiplets; [b] IR spectra recorded as a nujol mull unless otherwise stated; [c] NMR spectra recorded in CD_2Cl_2 unless otherwise stated; [d] IR spectra recorded as CH_2Cl_2 cast; [e] NMR spectra recorded in C_6D_6; [f] dppm bound phenyl groups omitted; [g] CO bands obscured by (12a); [h] characterized via low temperature NMR.

of THF. The solution was stirred for 18 h and then the solvent was removed in vacuo. The residue was redissolved in 5 mL of benzene, filtered through Celite and then 15 mL of a 2:1 mixture of Et_2O:n-pentane was added. After stirring for 1 h, the solvent was removed via cannula and the orange solid washed with 3×10 mL of the Et_2O:pentane mixture. Yield 31 mg, 29%. Anal. Calcd. for $C_{58}H_{49}P_4O_5RhMo$: C, 61.50%; H, 4.36%. Found: C, 61.41%; H, 4.52%.

(d) [RhMo(H_2C=CCO_2Me)$(CO)_4$$(dppm)_2$] (7). 40 µL (0.450 mmol) of methyl propiolate was added to a solution of 100 mg (0.0925 mmol) of compound **1** in 10 mL of THF. The solution was stirred for 18 h and the solvent was removed in vacuo. The residue was redissolved in 10 mL of benzene and filtered through Celite. Slow addition of 15 mL of Et_2O resulted in the formation of an orange precipitate which was then washed with 3×10 mL of Et_2O and dried in vacuo. Yield 54 mg, 50%. Anal. Calcd. for $C_{58}H_{49}F_6P_4O_6RhMo$: C, 59.81%; H, 4.24%. Found: C, 59.24%; H, 3.88%.

(e) [RhMo(CH=CH_2)$(CO)_4$$(dppm)_2$] (8). 1.5 mL of CH_2=CHMgBr (1.0 M in THF, 1.5 mmol) was added to a suspension of 233 mg of compound **2** (0.209 mmol) in 100 mL of benzene and stirred for 1.5 h. The dark red-brown solution was washed with 5×10 mL of degassed water, followed by solvent removal in vacuo. The residue was extracted with 2×5 mL of CH_2Cl_2 and the extracts filtered through Celite. Slow addition of 25 mL of a 1:1 mixture of Et_2O:n-pentane resulted in the formation of a yellow microcrystalline solid. The solvent was removed via cannula and the solid was washed with 3×5 mL of a 1:1 Et_2O:n-pentane, then dried in vacuo. Yield 153 mg, 66%. Anal. Calcd. for $C_{56}H_{47}P_4O_4RhMo$: C, 60.78%; H, 4.28%. Found: C, 60.70%; H, 4.04%.

(f) [RhW(CH=CH_2)$(CO)_4$$(dppm)_2$] (9). 0.810 mL of CH_2=CHMgBr (1.0 M in THF, 0.810 mmol) was added to 140 mg (0.116 mmol) of compound **3** in 45 mL of benzene and was then stirred for 1 h, during which time the solution turned from green to red. The solution was washed with 6×10 mL of degassed water then the solvent was removed in vacuo. The orange residue was dissolved in 10 mL of CH_2Cl_2 and filtered through Celite. An orange solid was precipitated by the addition of 25 mL of a 60:40 mixture of n-pentane:Et_2O. Yield 110 mg, 79%. Anal. Calcd. for $C_{56}H_{47}P_4O_4RhW$: C, 56.30 %; H, 4.00 %. Found: C, 55.93 %; H, 3.90 %.

(g) [RhMo(CH_3)(CO)$_4$(dppm)$_2$] (10). 225μL of CH_3MgCl (3.0 M in THF, 0.825 mmol) was added to a suspension of 150 mg of compound **2** (0.135 mmol) in 15 mL of benzene. The mixture was stirred for 3 h, during which time the orange solid dissolved and a dark red-brown solution formed. The solution was washed with 5×10 mL of degassed water, then concentrated in vacuo to *ca.* 5 mL. Hexanes were added dropwise to precipitate a yellow solid which was washed with 3×5 mL of hexanes and dried in vacuo. Yield 90mg, 61%. Anal. Calcd. for $C_{55}H_{47}P_4O_4RhMo$: C, 60.34%; H, 4.33%. Found: C, 60.18%; H, 4.26%.

(h) [RhMo(η^1-$CH_2CH=CH_2$)(CO)$_4$(dppm)$_2$] (11). 1.3 mL of 2.0 M $CH_2=CH$-CH_2MgCl (2.6 mmol) was added to 85 mg (0.0762 mmol) of compound **2** in 5 mL of benzene and stirred for 30 min. 95 mL of benzene was added and then the solution was washed with 5×10 mL of water, and the solvent was removed in vacuo. The residue was extracted with 2×5 mL of benzene, the extracts were filtered through Celite then 15 mL of n-pentane was added slowly to precipitate an orange solid. Yield 35 mg, 40%. Anal. Calcd. for $C_{57}H_{49}P_4O_4RhMo$: C, 61.09%; H, 4.41%. Found, C, 61.28%; H, 4.24%.

(i) [RhMo($CH_2C_6H_5$)(CO)$_4$(dppm)$_2$] and **[RhMo(C(O)$CH_2C_6H_5$)(CO)$_4$-(dppm)$_2$] (12 and 13).** 320 μL of 2.0 M benzylmagnesium chloride (0.640 mmol) was added to 100 mg (0.0897 mmol) of compound **2** in 100 mL of benzene under an atmosphere of CO. The solution was stirred under CO for 10 min then for 50 min with a gentle argon purge. After washing the solution with 5×10 mL of water the solvent was removed in vacuo. The residue was redissolved in 5 mL of CH_2Cl_2, filtered through Celite, then an orange solid was precipitated by the addition of 10 mL of 1:1 n-pentane:Et_2O. The solid was washed with 3x5 mL of the pentane/Et_2O mixture and dried in vacuo. Yield 67 mg. Extraction of this mixture with benzene/Et_2O (10:1) allowed the isolation of *ca.* 10 mg of **12**. Anal. Calcd. for $C_{61}H_{51}P_4O_4RhMo$: C, 62.20%; H, 4.30%. Found, C, 62.20%; H, 4.55%.

(j) [RhMoPh(CO)$_4$(dppm)$_2$] (14). 1.6 mL of 2.0 M PhMgCl (3.2 mmol) was added to 134 mg of compound **2** (0.108 mmol) in 100 mL of benzene under an atmosphere of carbon monoxide, resulting in the immediate formation of a dark brown solution. The solution was stirred under an atmosphere of CO for 10 min then with a gentle argon purge for 50 min. The solution was washed with 5×10mL of degassed water followed by solvent removal in vacuo. After redissolving in 5 mL of CH_2Cl_2, the solution was filtered through Celite. An orange solid was precipitated by the addition of 30 mL of a 1:1 mixture of Et_2O:n-pentane and the solvent removed via cannula. The solid was washed with 3×5 mL of Et_2O:n-pentane and dried in vacuo. Yield 55 mg, 40%. NMR spectra showed that the complex crystallized with 1/4 mol of CH_2Cl_2. Anal. Calcd. for $C_{60.25}H_{49.5}P_4O_4RhMo$: C, 61.43%; H, 4.24%; Cl, 2.08%. Found: C, 61.68%; H, 4.20%; Cl, 1.51%.

(k) [RhMo(=CH(CH$_3$))(CO)$_4$(dppm)$_2$][BF$_4$] (15). This compound was characterized via low-temperature NMR spectroscopy. 1.5 µL of $HBF_4{\bullet}(OMe_2)_2$ (0.014 mmol) was added to 15.4 mg (0.014 mmol) of compound **8** in 0.5 mL of CD_2Cl_2 in a septum-capped NMR tube at -80 °C, resulting in the immediate formation of a purple solution. NMR spectra of the reaction mixture were obtained at temperatures starting from -80 °C to 25 °C by warming the probe to the desired temperature, with the sample in place, and allowing the sample to stand for 20 min before recording the spectra.

(l) [RhMo(η^2-H_2C=CH_2)(CO)$_4$(dppm)$_2$][BF$_4$] (16). 3 µL (0.028 mmol) of HBF_4•$(OMe_2)_2$ was added to a solution of 25 mg (0.0226 mmol) of compound **8** in 5 mL of CH_2Cl_2 at -80 °C, resulting in the formation of a deep purple solution, which slowly turned brown upon warming to room temperature over a period of 1 h. 7 mL of Et_2O was added, resulting in the formation of a brown solid. The solvent was removed via cannula and the solid was washed with 3×10 mL of Et_2O and dried in vacuo. Yield 19 mg, 70 %. Elemental analyses were not obtained due to the unstable nature of the compound.

(m) [RhW(=CHCH$_3$)(CO)$_4$(dppm)$_2$][BF$_4$] (17). This compound was characterized via low-temperature NMR spectroscopy. 1.6 µL of HBF_4•$(OMe_2)_2$ (0.0131 mmol) was added to 13.9 mg (0.0116 mmol) of compound **9** in 0.5 mL of CD_2Cl_2 in a septum-capped NMR tube at -80 °C, resulting in the immediate formation of a purple solution. NMR spectra of the reaction mixture were obtained at temperatures starting from -80 °C to 25°C by warming the probe to the desired temperature, with the sample in place, and allowing the sample to stand for 20 min before recording the spectra.

(n) [RhW(η^2-CH_2=CH_2)(CO)$_4$(dppm)$_2$][BF$_4$] (18). 4.1 µL of HBF_4•$(OMe_2)_2$ (0.0337 mmol) was added to 40 mg (0.0335 mmol) of compound **9** in 5 mL of CH_2Cl_2 at -80 °C. The solution was warmed to room temperature during which time it turned brown. 25 mL of Et_2O was added slowly, resulting in the formation of a brown precipitate. The solid was washed with 2×10 mL of Et_2O and dried briefly under vacuum. Yield 30 mg, 70 %. Elemental analyses were not obtained due to the unstable nature of the compound.

(o) [RhMo(PhC$_2$H)(CO)$_4$(dppm)$_2$][BF$_4$] (19). 3 µL of HBF_4•$(OMe_2)_2$ (0.0246 mmol) was added to a solution of 25 mg (0.0226 mmol) of compound **8** in 5 mL of CH_2Cl_2 at -80 °C. The solution was warmed to -60 °C then 38 µL (0.346 mmol) of phenylacetylene was added. The solution was warmed to room temperature and stirred for 1 h then 15 mL of Et_2O were added resulting in the formation of a green solid. The solvent was removed via cannula and the solid washed with 2×10 mL of Et_2O and dried in vacuo. Yield 24 mg, 89%. Anal. Calcd. for $C_{62}H_{50}BF_4P_4O_4RhMo \cdot 0.5CH_2Cl_2$: C, 57.26%; H, 3.92%. Found, C 57.49%, H 3.72%. The presence of half an equivalent of CH_2Cl_2 was confirmed by ^1H NMR.

X-ray Data Collection. X-ray data collection and structure solution were carried out by Dr. R. McDonald. Suitable crystals of compound **2** were grown by slow diffusion of Et_2O into a CH_2Cl_2 solution of **2** at ambient temperature. Data were collected to a maximum $2\theta = 50.0°$ on an Enraf-Nonius CAD4 diffractometer using Mo $K\alpha$ radiation at 22 °C. Unit cell parameters were obtained from a least-squares refinement of the setting angles of 54 reflections in the range $21.2° < 2\theta < 23.8°$. The cell parameters and systematic absences suggested $P2_1/c$ (no. 14) as the space group. Three reflections were chosen as intensity standards and were remeasured every 7200 sec of X-ray exposure time, with no decay evident. Absorption corrections were applied to the data by the method of Walker and Stuart.[13] See Table 2.2 for a summary of crystal data and X-ray collection information.

The structure was solved by direct methods, using SHELX-86[14] to locate the Rh, Mo, and P atoms. All other atoms were located after subsequent least-squares cycles and difference Fourier syntheses. Refinement was completed using the program SHELXS-93.[15] All hydrogen atoms of the complex were included as fixed contributions; their idealized positions were generated from the geometries of the attached carbon atoms and their thermal parameters set at 20% greater than the isotropic thermal parameter of these carbons. The partial-occupancy CH_2Cl_2 solvent molecules were refined with fixed idealized geometries: d(Cl(91)–C(91)) = d(Cl(92)–C(91)) = d(Cl(93)–C(92)) = d(Cl(93)–

Table 2.2 Crystallographic Experimental Details for Compound **2**•0.75 CH_2Cl_2.

A. Crystal Data	
formula	$C_{54.75}H_{45.5}Cl_{2.5}MoO_4P_4Rh$[a]
formula weight	1178.77
crystal system	monoclinic
space group	$P2_1/c$ (No. 14)
unit cell parameters	
a (Å)	12.940 (3)
b (Å)	27.149 (4)
c (Å)	15.3860 (14)
β(deg)	95.955 (13)
V (Å^3)	5376.3 (16)
Z	4
ρ_{calcd} (g cm^{-3})	1.456
μ (mm^{-1})	0.827
B. Data Collection and Refinement Conditions	
diffractometer	Enraf-Nonius CAD4
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	22
scan type	θ–2θ
data collection 2θ limit (deg)	50.0
total data collected	9852 ($0 < h < 15$, $0 < k < 32$, $-18 < l < 18$)
independent reflections	9408
number of observations (*NO*)	6730 ($F_o^2 > 2\sigma(F_o^2)$)
structure solution method	direct methods (*SHELXS–86*)
refinement method	full-matrix least-squares on F^2 (*SHELXL–93*)
absorption correction method	*DIFABS*
range of absorption correction factors	1.090–0.815
data/restraints/parameters	9402 [$F_o^2 > -3\sigma(F_o^2)$]/6/604
goodness-of-fit (S)[b]	1.017 [$F_o^2 > -3\sigma(F_o^2)$]
final R indices[c]	
$F_o^2 > 2\sigma(F_o^2)$	**R_1 = 0.0369,** wR_2 = 0.0938
all data	R_1 = 0.0753, **wR_2 = 0.1125**
largest difference peak and hole	0.652 and –0.545 e Å^{-3}

[a] for [RhMo(CO)$_4$(μ-Cl)(dppm)$_2$]•0.75 CH_2Cl_2

[b] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0525P)^2 + 6.8113P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

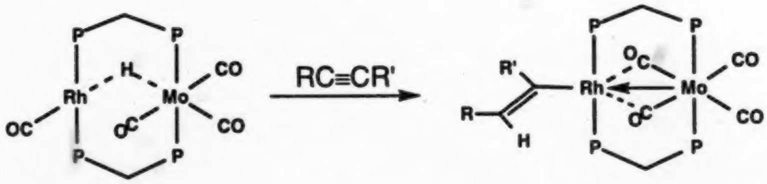
[c] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

$C(92)) = 1.80(1)$ Å; $d(Cl(91)^{\circ}Cl(92)) = d(Cl(93)^{\circ}Cl(94)) = 2.95(1)$ Å. The final model for the complex refined to values of $R_1(F) = 0.0369$ (for $F_o^2 \geq 2\sigma(F_o^2)$) and $wR_2(F^2) = 0.1125$ (for all data with $F_o^2 > -3\sigma(F_o^2)$).

Results and Compound Characterization.

Preparation of Alkyl and Alkenyl Complexes. Transition-metal complexes containing σ-bound organic fragments occupy key positions as intermediates in many catalytic sequences.[16] These complexes may be prepared in a variety of ways, including reactions of metal-hydride complexes with alkynes and via halide displacement with organic nucleophiles. Our investigation into alkyl and alkenyl complexes of Rh and group VI metals began with the preparation of a variety of vinyl species, *via* the reaction of the known hydride, $[RhMo(\mu\text{-}H)(CO)_4(dppm)_2]$ (**1**),[11] with activated alkynes. Reaction of compound **1** with dimethyl acetylenedicarboxylate (DMAD), produces $[RhMo(MeO_2CC{=}C(H)CO_2Me)(CO)_4(dppm_2)]$ (**4**) in high yield. The $^{31}P\{^1H\}$ NMR spectrum of this complex shows two resonances at 23.9 ppm and 38.9 ppm in which the high-field signal has a doublet coupling of 136 Hz, which is typical for rhodium-phosphorus coupling. The ^1H NMR spectrum of **4** shows the DMAD methyl groups, apparently coincidently degenerate, at 3.05 ppm and the vinylic hydrogen resonating at 4.56 ppm as a doublet with 2.5 Hz coupling to Rh, indicating that the alkenyl moiety is bound to Rh. The small rhodium-hydrogen coupling constant suggests that these two groups are in a mutually cis arrangement about the carbon-carbon double bond, as is often observed for alkyne insertions into metal-hydrogen bonds. The IR spectrum of **4** in the solid state shows terminal CO bands at 1966 and 1911 cm^{-1}, as well as bands at 1771 and 1749 cm^{-1}, suggesting the presence of bridging carbonyls, and DMAD carbonyl bands at 1700 cm^{-1}. In the $^{13}C\{^1H\}$ NMR spectrum of this compound, four carbonyl resonances appear at 208.3, 220.1, 235.1 and 247.5 ppm. All of these signals are broadened singlets (*ca.* 25 Hz half width) except for the low-field resonance which displays rhodium coupling of 24.5 Hz. Surprisingly, these carbonyls display no resolvable ^{31}P coupling; however, this seems typical of the alkyl and alkenyl Rh-Mo complexes prepared in this work, and may be a consequence of the presence of quadrupolar isotopes of molybdenum (^{95}Mo and ^{97}Mo, I = 5/2 with *ca.* 16% and 10% natural abundance, respectively). This lack of coupling has been observed in other dppm-bridged binuclear systems containing the Rh/Mn combination of metals and was attributed to the presence of quadrupolar isotopes of manganese.[17a] The Rh-C coupling constant and the low CO stretching frequencies suggest a semibridging bonding mode in which the CO is bound more strongly to Mo and weakly to Rh. This can be compared to a symmetrically bridging arrangement, for which the Rh-C coupling generally exceeds 30 Hz.[17b] The presence of two low frequency CO bands in the IR spectrum suggests that in the solid state both carbonyls are bound terminally to molybdenum with weak semibridging interactions with rhodium. That only one CO resonance displays rhodium coupling in the ^{13}C{^{1}H} NMR spectrum suggests that one of the carbonyls directed towards the rhodium center engages in a stronger semibridging interaction with this metal than the other. This may be a consequence of steric factors, where the bulky vinyl group forces the CO syn to this substituent away from the rhodium center, with the CO anti to the vinyl group compensating by accepting more electron density from the rhodium center.

The presence of semibridging carbonyls is typical of binuclear complexes having an η^1-hydrocarbyl ligand bound to rhodium. For example, in the closely related alkenyl complex [$RhOs(C(CH_3)=CH_2)(CO)_3(dppm_2)$], a semibridging interaction was proposed based on spectroscopic data and confirmed crystallographically.[4b] The presence of semibridging carbonyls in such species is presumably necessary to alleviate the buildup of electron density on rhodium resulting from the presence of the two phosphines and the alkenyl group, since in this series of compounds rhodium has no strong π-acceptor ligands of its own. Analysis of the above spectroscopic data indicates that compound **4** consists of a σ-bound alkenyl group on rhodium and four carbonyls bound to molybdenum, one of which is engaging in a weak semibridging interaction with rhodium. In order to give rhodium a favourable 16e configuration, a Mo→Rh dative bond is invoked. An alternate view of the bonding would involve a "classical" metal-metal bond and a symmetrically-bridged carbonyl. However, our experience with Rh-CO coupling constants suggests that the semibridging formulation is more appropriate.[4-6] In all the Rh/Mo hydrocarbyl species prepared in this study, it was found that the organic fragment was always bound to the rhodium center in the geometry shown below.



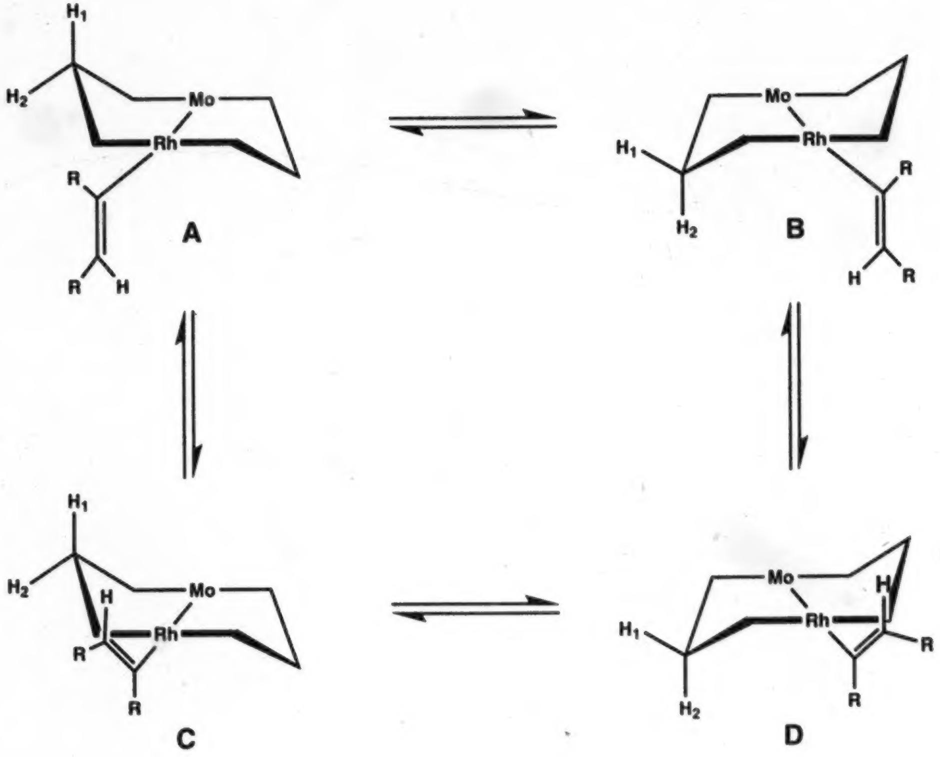
(1)

(4) R = R' = CO$_2$Me
(5) R = R' = CF$_3$
(6) R = H, R' = C(O)Me
(7) R = H, R' = CO$_2$ Me

A similar arrangement has been observed in the Rh/Os,[4a,b] and Rh/Ru[5] alkyl complexes previously prepared in this group but is in contrast to a number of Rh/Ir complexes, in which the hydrocarbyl group is usually bound to iridium.[3]

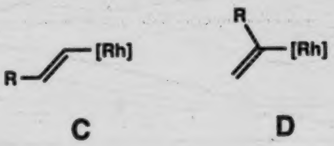
Reaction of **1** with hexafluoro-2-butyne (HFB) produces [RhMo(F$_3$CC=C(H)-CF$_3$)(CO)$_4$(dppm)$_2$] (**5**), which is spectroscopically similar to **4**. The ^{31}P{^{1}H} NMR resonances are centered at 38.7 ppm for the Mo-bound phosphorus and at 22.0 ppm for the Rh-bound phosphorus nuclei, with a typical Rh-P coupling constant of 133 Hz for the latter. The IR spectrum of this compound shows three CO bands at 1978, 1923 and 1788 cm^{-1}, indicative of terminal and bridging carbonyls. The ^1H NMR spectrum shows the vinylic-hydrogen resonance at 5.15 ppm as a slightly broadened quartet, in which the quartet structure is due to ^{19}F coupling (10 Hz) and the broadening is likely a result of unresolved Rh coupling. In the ^1H NMR spectrum, the dppm methylene hydrogen resonances appear as two multiplets, indicating separate environments for these protons due to apparent front-back asymmetry in the planar $RhMoP_4$ framework. The source of the asymmetry is presumably the orientation of the vinyl group, and suggests that rotation of the substituted vinyl group is hindered, presumably due to interactions of the vinyl substituents and the large phenyl groups on the dppm ligands. As shown in Scheme 2.1, exchange of H_1 and H_2 between axial and equatorial positions in the transformation from **A** to **B** does not exchange the chemical environments for these hydrogens because in structure **A** H_1 is pointing away from the vinyl substituent whereas in structure **B** H_2 is pointing in the same direction as this vinyl group. However, if vinyl group rotation were to accompany axial-equatorial exchange of the dppm methylene hydrogens (which does not appear to occur on the NMR time scale in compound **5**), as shown in the transformation from **A** to **D**, then H_1 in **A** would become equivalent to H_2 in **D**, because in these orientations both axial hydrogens are pointing away from the vinyl group. This fluxionality would result in equilibration of the methylene hydrogen environments and as a result the methylene signal would appear as a pseudoquintet, due to coupling to the four phosphorus nuclei. Presumably, the equilibration of these methylene protons would be observed at higher temperatures.

Scheme 2.1. Fluxionality in Vinyl Species


H₁
H₂
Mo
Rh
R
R
H
A
B
C
D

Hindered rotation of vinyl groups has been observed in other vinyl species prepared in our group.[4b] For example, below 0 °C the dppm-methylene region in the ^{1}H NMR spectrum of [RhOs(C(CH$_3$)=CH$_2$)(CO)$_3$(dppm)$_2$] displays an AB quartet (due to H-H coupling with superimposed ^{31}P coupling) for the dppm methylene hydrogens, indicating that the vinyl group rotation is slow on the NMR time scale. Upon warming, the methylene signal broadens and coalesces to a sharp quintet at 75 °C, presumably because rotation of the vinyl group is giving the same average environment on each side of the RhOsP$_4$ plane.

Another alkenyl-containing species in this series is obtained by the reaction of 3-butyn-2-one with **1**, to give [RhMo(CH$_3$C(O)C=CH$_2$)(CO)$_4$(dppm)$_2$] (**6**). With this unsymmetrical alkyne, two regioisomers are possible, as shown in **C** and **D** below.



R = C(O)CH$_3$

The ^{1}H NMR spectrum of this species shows the methyl singlet at 1.13 ppm and the dppm methylene resonance at 2.95 ppm as a broad AB quartet with additional phosphorus coupling. A slightly broadened singlet is observed at 5.36 ppm and a doublet, with 4.3 Hz Rh coupling, at 5.59 ppm is also apparent. If isomer **C** were formed, it is expected that the hydrogens on the α and β carbon of the vinyl group would show a large trans coupling of 15 to 18 Hz.[18] The lack of this coupling in the ^{1}H NMR spectrum of **6** indicates that the less sterically favourable regioisomer, **D** is formed. This presumably is due to the formation of a stronger metal-carbon bond in **D**, due to the presence of the electron withdrawing C(O)CH$_3$ group on this carbon. Formation of the less sterically favourable product has been observed previously when the resulting product has electron-withdrawing substituents on the α-carbon.[19] The vinyl-containing species [RhMo(C(CH$_3$CO$_2$)=CH$_2$)(CO)$_4$(dppm)$_2$] (7) is prepared similarly, via the reaction of 1 with methyl propiolate. The spectroscopic properties for 7 are very similar to those presented above and will not be discussed here.

Attempts to obtain an unsubstituted vinyl-containing species via the reaction of 1 with acetylene were unsuccessful. Although this reaction did result in the formation of some of the desired product, it was accompanied by a variety of uncharacterized impurities. This was also observed in the reaction of [RhOs(CO)$_3$(H)(dppm)$_2$] with acetylene,[4b] and is not surprising due to the propensity of acetylene to undergo a variety of reactions such as oligomerization, and formation of vinylidenes.[20]

Another common method for placing hydrocarbyl groups on transition metals involves the reaction of the appropriate metal-halide species with main-group organometallics such as alkyllithium or Grignard reagents. The known chloride species [RhMo(μ-Cl)(CO)$_4$-(dppm)$_2$] (2) seemed to be a convenient precursor for this chemistry. However, before embarking on this chemistry, we felt obliged to complete the characterization of the complex, since there was ambiguity in the literature about its structure,[12a, b] as will be discussed later. An X-ray structure of 2, shown in Figure 2.1, confirms the normal "A-frame" geometry for the complex in which the chloro ligand bridges the two metals. In this arrangement the geometry at Rh is square planar, characteristic of Rh(+1), and at Mo is octahedral, characteristic of Mo(0). We view the chloro ligand to be bound as an anion to rhodium, while simultaneously donating a lone pair of electrons to molybdenum to complete the valence shell of this metal. The substantially shorter Rh-Cl (2.416(1) Å) compared to the Mo-Cl (2.651(1) Å) bond length is consistent with a Rh(+1)/Mo(0) formulation, on the basis of an expected smaller radius of Rh(+1) compared to Mo(0) (see Tables 2.3 and 2.4 for selected bond lengths

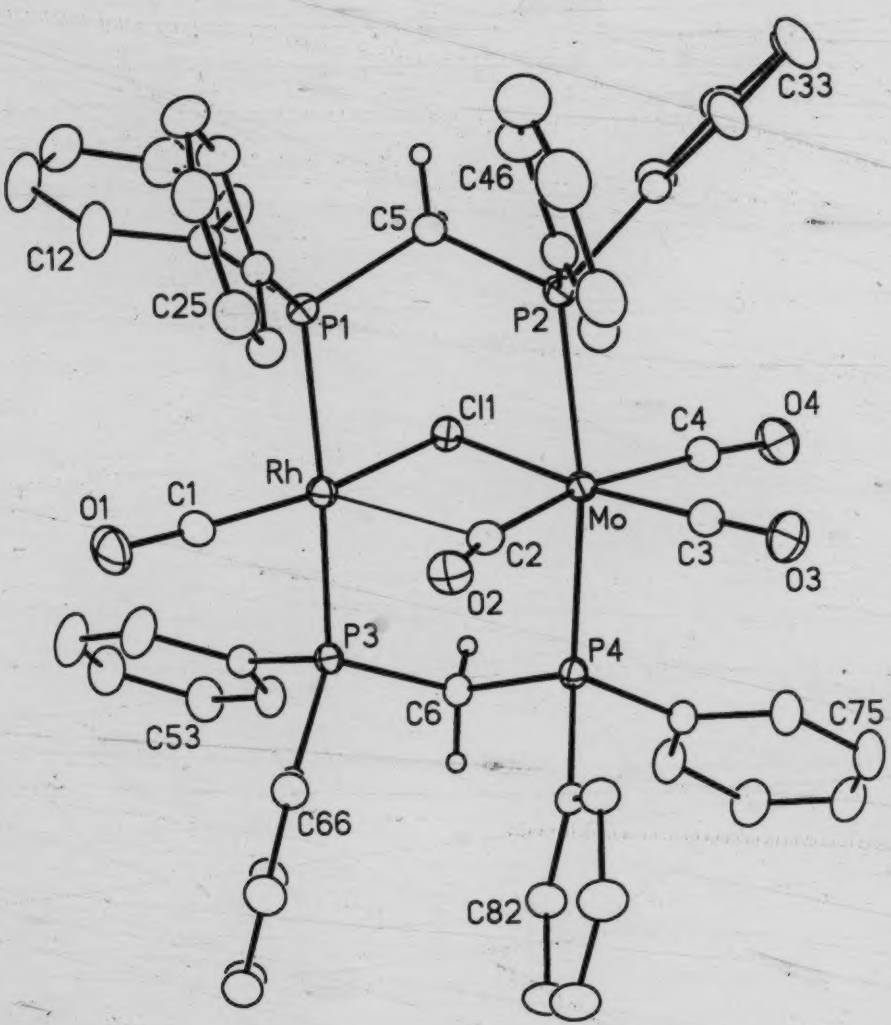

C33
C46
C5
C12
C25
P1
P2
Cl1
O4
C4
Rh
C1
O1
Mo
C2
C3
O3
O2
P3
P4
C6
C53
C75
C66
C82

Figure 2.1 Perspective view of the [RhMo(CO)$_4$(μ-Cl)(dppm)$_2$] (**2**) molecule showing the atom labelling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters for the dppm methylene groups, and are not shown for the dppm phenyl groups.

Table 2.3. Selected Interatomic Distances (Å) for $[RhMo(CO)_4(\mu\text{-}Cl)(dppm)_2]$ (**2**)

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Rh	Cl(1)	2.4163(12)	Mo	C(4)	2.024(5)
Rh	P(1)	2.3127(12)	P(1)	C(5)	1.836(4)
Rh	P(3)	2.3212(11)	P(2)	C(5)	1.854(4)
Rh	C(1)	1.807(5)	P(3)	C(6)	1.833(4)
Mo	Cl(1)	2.6511(12)	P(4)	C(6)	1.847(4)
Mo	P(2)	2.4786(12)	O(1)	C(1)	1.141(5)
Mo	P(4)	2.4758(12)	O(2)	C(2)	1.155(5)
Mo	C(2)	2.021(5)	O(3)	C(3)	1.170(6)
Mo	C(3)	1.919(5)	O(4)	C(4)	1.140(6)

Table 2.4. Selected Interatomic Angles (deg)

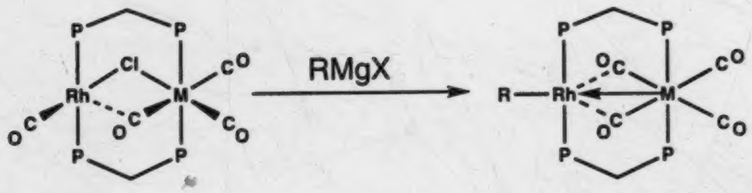
Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
Cl(1)	Rh	P(1)	88.95(4)	P(4)	Mo	C(3)	93.94(14)
Cl(1)	Rh	P(3)	86.97(4)	P(4)	Mo	C(4)	89.59(14)
Cl(1)	Rh	C(1)	165.5(2)	C(2)	Mo	C(3)	83.8(2)
P(1)	Rh	P(3)	170.64(4)	C(2)	Mo	C(4)	165.1(2)
P(1)	Rh	C(1)	89.56(15)	C(3)	Mo	C(4)	81.6(2)
P(3)	Rh	C(1)	92.28(15)	Rh	Cl(1)	Mo	77.74(3)
Cl(1)	Mo	P(2)	85.75(4)	Rh	P(1)	C(5)	112.90(15)
Cl(1)	Mo	P(4)	87.40(4)	Mo	P(2)	C(5)	112.97(15)
Cl(1)	Mo	C(2)	105.78(13)	Rh	P(3)	C(6)	114.24(14)
Cl(1)	Mo	C(3)	170.38(15)	Mo	P(4)	C(6)	112.21(14)
Cl(1)	Mo	C(4)	88.92(15)	Rh	C(1)	O(1)	177.0(5)
P(2)	Mo	P(4)	171.39(4)	Mo	C(2)	O(2)	165.2(4)
P(2)	Mo	C(2)	88.08(13)	Mo	C(3)	O(3)	179.1(5)
P(2)	Mo	C(3)	93.68(14)	Mo	C(4)	O(4)	171.7(5)
P(2)	Mo	C(4)	95.49(14)	P(1)	C(5)	P(2)	115.0(2)
P(4)	Mo	C(2)	88.77(13)	P(3)	C(6)	P(4)	114.1(2)

and angles). Consistent with this view, all bonds associated with Rh are shorter than the analogous bonds in Mo. For example, the average Rh-P distance (*ca.* 2.32 Å) is substantially shorter than the average Mo-P distance (*ca.* 2.48 Å) and the shortest metal-carbonyl distance is also that involving Rh. The carbonyl groups on Mo show the expected trends, with that opposite the donor chloride ligand having the shortest Mo-CO distance (1.919(5) Å), whereas the two mutually trans carbonyls have long Mo-CO distances (2.024(5) Å and 2.021(5) Å) due to decreased π back donation resulting from competition for π-electron density. The carbonyl (C(2)O(2)) in the vicinity of rhodium appears to be involved in a weak semibridging interaction with this metal as seen from the non-linearity of this group (Mo-C(2)-O(2) = 165.2(4)°) and by the large asymmetry in its distances to the two metals (Mo-C(2) = 2.021(5) Å; Rh-C(2) = 2.720(5)Å). However, the rather long distance to rhodium, and the carbonyl bending, which is about 10 ° less than in semibridging carbonyls having a more substantial interaction with rhodium indicates a very weak interaction in the present case. By comparison, in the compounds $[RhMn(CO)_4(\mu\text{-}S)(dppm)_2]^{21}$ and $[RhOs(C(CH_3)=CH_2)(CO)_3(dppm)_2]$,[4b] the Rh-CO interaction of the semibridging CO is 2.214(5) Å and the Mn-C-O angle is 149.9(4) ° in the former, with the corresponding values in the Rh/Os complex being 2.075(8) Å and 155.2(6) °. The Rh-Mo separation, at 3.1852(7) Å, indicates no metal-metal bond is present, and consequently is longer than the P-P separations (3.113(2), 3.089(2) Å) within the diphosphine ligands.

The presence of a bridging chloride in **2** suggested the possibility that substitution of this halide by a hydrocarbyl group may give rise to an interesting hydrocarbyl-bridged species. Certainly, this had not been observed with the alkenyl ligands, which were all terminally bound to rhodium, possibly due to unfavourable steric interactions of the substituents on the alkenyl ligands with either the surrounding ligands on molybdenum or with the dppm phenyl groups. It was felt that a compound containing a bridging-alkyl group might be obtained with a smaller alkyl ligand such as a methyl group, so a variety of halide metathesis reactions were carried out with organomagnesium reagents in order to test this possibility.

For the purpose of comparison to the previously prepared alkenyl species and in view of the relevance of vinyl species to Fischer-Tropsch chemistry,[22] the first halide metathesis reaction performed with **2** was with vinylmagnesium chloride, as shown in Scheme 2.2. This reaction produced [RhMo(CH=CH$_2$)(CO)$_4$(dppm)$_2$] (**8**), which could not be obtained cleanly in the previous reaction of [RhMo(CO)$_4$(μ-H)(dppm)$_2$] with acetylene. The resulting unsubstituted vinyl species has ^{1}H NMR signals at 4.27, 5.09 and 6.75 ppm for the hydrogens cis or trans to rhodium, and the hydrogen on the α-carbon, respectively, having the expected cis and trans hydrogen-hydrogen couplings of 11 Hz and 18 Hz. The dppm methylene region of the ^{1}H NMR spectrum differs from the previously mentioned substituted vinyl species in that only one signal (a pseudoquintet) is observed, suggesting that equilibration of the axial and equatorial hydrogens is occurring through rapid rotation of the vinyl group about the vinyl-rhodium bond, presumably reflecting the lower steric demands of the unsubstituted vinyl group (see Scheme 2.1). The IR spectrum of **8** shows carbonyl bands at 1968, 1919, 1776 and 1760 cm^{-1} with the lower frequency bands indicative of bridging interactions. These CO bands are shifted to lower energy than those of the previously mentioned vinyl species; for example, [RhMo(C(CF$_3$)=CH(CF$_3$))(CO)$_4$(dppm)$_2$] has metal-bound carbonyl bands at 1978, 1924, and 1788 cm^{-1}. In this HFB-derived complex the vinyl group is a poorer σ-donor, due to the presence of electron withdrawing CF$_3$ groups which result in less electron-rich metal centers and correspondingly less back donation to the carbonyl ligands, than is the case with the CH=CH$_2$ group in **8**.

Scheme 2.2. Preparation of Hydrocarbyl Complexes



(2)

R = CH=CH$_2$, M = Mo (**8**)
R = CH=CH$_2$, M = W (**9**)
R = CH$_3$, M = Mo (**10**)
R = η^1-C$_3$H$_5$, M = Mo (**11**)
R = CH$_2$Ph, M = Mo (**12**)
R = C(O)CH$_2$Ph, M = Mo (**13**)
R = Ph, M = Mo (**14**)

The tungsten-containing analogue, $[RhW(CH{=}CH_2)(CO)_4(dppm)_2]$ (**9**) was prepared in an similar manner and had comparable spectroscopic properties to compound **8** indicating it had a similar structure. This showed that even substituting tungsten, a third-row metal, for molybdenum, the hydrocarbyl ligand is favoured on rhodium rather than the group 6 metal, in spite of the stronger expected W-C *vs*. Mo-C bond.[23]

In order to determine if a smaller hydrocarbyl ligand would bind in a bridging position, much like the chloro group in the precursor (**2**), $[RhMo(CH_3)(CO)_4(dppm)_2]$ (**10**) was prepared via the reaction of compound **2** with methylmagnesium chloride. As with the alkenyl products, it was found that the methyl group was terminally bound to rhodium, as indicated by the ^1H NMR spectrum which showed a triplet of doublets at 0.15 ppm for the methyl resonance. The coupling constants for this signal (2.3 Hz rhodium coupling and 7.5 Hz phosphorus coupling to the two equivalent rhodium-bound phosphines) are quite similar to an isoelectronic complex $[RhRe(CH_3)(CO)_4(dppm)_2][OTf]$, the X-ray structure of which confirmed that the methyl group was terminally bound to rhodium.[6] The IR spectrum of **10** indicates that the complex has both terminal and bridging carbonyls, with bands at 1952, 1900, 1759 and 1743 cm^{-1}. The $^{13}C\{^1H\}$ NMR spectrum of this species has two resonances, at 216.4 and 247.8 ppm. As has been observed in many of the above mentioned Rh/Mo hydrocarbyl species, there is no observable coupling of either of these carbonyls with rhodium, but the large half-width (*ca.* 45 Hz) of the low-field resonance could easily mask a small rhodium-carbon coupling that is characteristic of a semibridging carbonyl.

Preparation of the benzyl analogue of **10** was of interest to us in view of the fact that other groups had successfully removed a hydrogen from a terminal benzyl ligand to form an alkylidene.[24] Our interest in carbene-like species stems from their importance in Fischer-Tropsch catalysis.[22] When a large excess of benzylmagnesium chloride was added to **2**, no alkylation products were obtained. However, if the reaction is performed with seven equivalents of the Grignard reagent under an atmosphere of carbon monoxide, two compounds are obtained in a 1:1.8 ratio. The major species, $[RhMo(CH_2Ph)(CO)_4(dppm)_2]$ (**12**) has $^{31}P\{^1H\}$ NMR signals at 41.4 ppm and 26.1 ppm, with the latter signal displaying rhodium coupling of 151 Hz, whereas the minor compound, $[RhMo(C(O)CH_2Ph)(CO)_4(dppm)_2]$ (**13**), has ^{31}P NMR chemical shifts of 40.9 and 17.3 ppm. The significant difference in the upfield chemical shift and the larger rhodium coupling of 168 Hz in **13** suggests a quite different chemical environment at the rhodium center. An inspection of the ^1H NMR spectrum of **12** reveals the benzyl methylene hydrogen resonance at 2.66 ppm as a doublet of triplets. The rhodium coupling of 3.6 Hz, and the 8.2 Hz coupling to the rhodium-bound phosphines indicates that the benzyl ligand is σ-bound to the rhodium center. In contrast to **12**, the resonance for the benzyl hydrogens in **13** appears as a singlet at 3.15 ppm, with no coupling to either rhodium or phosphorus. This suggests the presence of a phenylacetyl group bound to rhodium, resulting from attack of the Grignard reagent on a coordinated carbonyl, as will be discussed later in this chapter. Further evidence of this structure is obtained from the IR spectrum of **13**, which shows an acyl CO band at 1600 cm^{-1}. Note that this compound was always obtained as a minor species so the metal-bound carbonyl bands in the IR spectrum were always obscured by those of **12**.

An aryl complex, analogous to the η^1-hydrocarbyl complexes already described, can be prepared by the reaction of $[RhMo(CO)_4(\mu\text{-}Cl)(dppm)_2]$ (**2**) with phenylmagnesium chloride under a carbon monoxide atmosphere, yielding $[RhMo(Ph)(CO)_4(dppm)_2]$ (**14**). Unlike the reaction involving the benzyl Grignard, the reaction of **2** with phenylmagnesium chloride gave only the product resulting from apparent attack at rhodium, although attack at coordinated CO, followed by subsequent CO loss cannot be ruled out. Generally, the spectroscopy of this compound is similar to that of the compounds discussed above. Notable features are that no rhodium-coupling of the β-hydrogens of the metal-bound phenyl group is observed, and the metal-bound phenyl hydrogens are shifted upfield from the phenyl-hydrogen resonances of the dppm-bound phenyl groups, presumably due to the proximity of this group to the rhodium center.

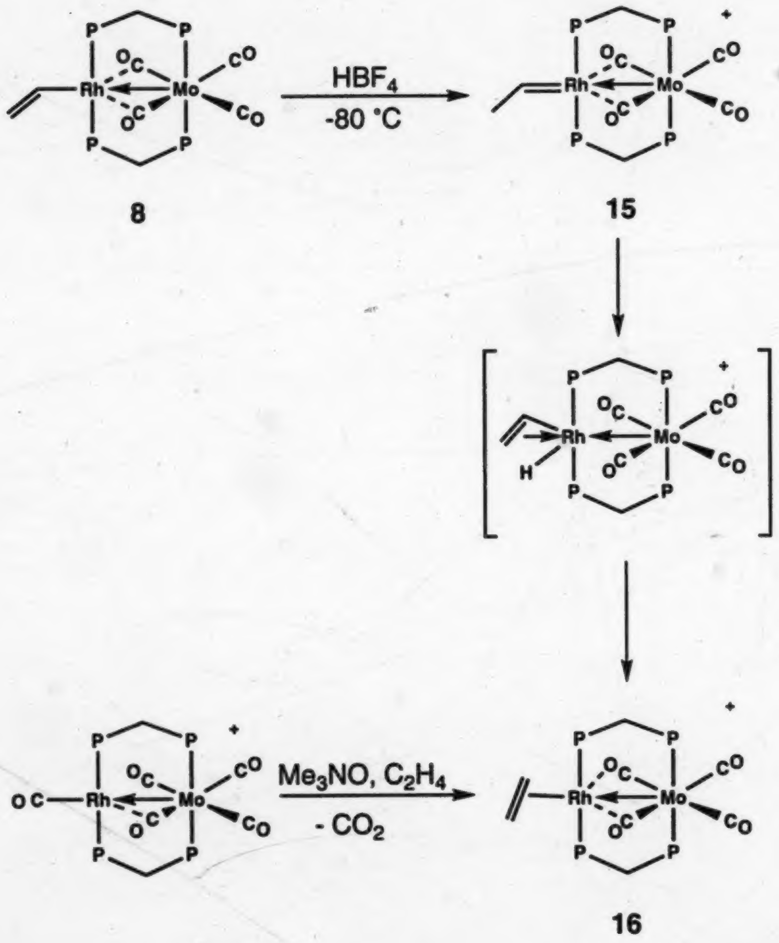
As was mentioned previously, one of the key steps in a mechanism recently proposed by the Maitlis group for hydrocarbon chain lengthening in the Fischer-Tropsch process is the migration of a vinyl moiety to a surface-bound methylene, forming an allyl group.[22] Accordingly, we set out to prepare the allyl-containing species [RhMo(C_3H_5)-$(CO)_4$(dppm)$_2$] **(11)** via the reaction of **2** with allylmagnesium chloride. It had been found that the analogous species [RhOs(η^3-C_3H_5)$(CO)_3$(dppm)$_2$] contained an η^3-allyl ligand[4b] and it was of interest to determine if a similar Rh/Mo compound could be prepared. Addition of excess allylmagnesium chloride to **2** resulted in the formation of [RhMo(η^1-C_3H_5)$(CO)_4$(dppm)$_2$] **(11)**, the ^{1}H NMR spectrum of which showed the α-hydrogens of the η^1-allyl group resonating at 2.74 ppm. This signal is a multiplet, with unresolved rhodium, ^{31}P and β-H coupling. The β-H signal is a multiplet at 5.87 ppm with typical cis and trans couplings of 9 and 17 Hz to the other olefinic hydrogens, which appear as doublets at 4.10 and 3.46 ppm. The chemical shifts for η^3-allyl hydrogens are generally in the range of 1-3 ppm for H_{anti}, 2-5 ppm for H_{syn} and 4-6.5 ppm for $H_{central}$ with coupling between H_c and H_s or H_a of 7-11 Hz. The allylic hydrogen chemical shifts and H-H coupling constants for **11** indicate the allyl group is η^1 bound, as does the lack of observable rhodium and ^{31}P coupling to any but the α-hydrogens. All other spectral parameters for **11** suggested a structure much like those discussed previously.

Reactivity of Hydrocarbyl Complexes

One of the goals of this project was to prepare dialkyl or alkyl-hydrido complexes via the reaction of neutral species with electrophiles, and to investigate the effects of an adjacent metal on a variety of reaction types, including reductive eliminations. These neutral alkyl complexes were found, for the most part, to be quite unreactive towards a variety of reagents as will be discussed later in this chapter.

The logical starting point for the investigation of the reactivity of these complexes towards electrophiles seemed to be with $[RhMoCH_3(CO)_4(dppm)_2]$ (**10**) because of its simple spectroscopic features. The reaction of **10** with HBF_4 was followed by variable-temperature NMR spectroscopy, and no reaction was observed until the reaction mixture was warmed to 10 °C, at which point the known compound, $[RhMo(CO)_5(dppm)_2][BF_4]$ was formed along with various decomposition products. No intermediates were observed, and the reasons for this will be addressed in the discussion section of this chapter. In contrast to the inertness of the methyl compound **10** to acid at low temperature, protonation of $[RhMo(CH{=}CH_2)(CO)_4(dppm)_2]$ (**8**) with HBF_4 at -80 °C, results in an immediate color change from yellow to purple. $^{31}P\{^1H\}$ NMR spectroscopy showed the presence of a new compound, characterized as $[RhMo({=}CH(CH_3)(CO)_4$-$(dppm)_2][BF_4]$ (**15**), and having ^{31}P NMR chemical shifts at 11.7 ppm ($^1J_{Rh\text{-}P} = 146$ Hz) and 39.4 ppm, for the rhodium- and molybdenum-bound phosphines, respectively. The ^1H NMR spectrum of this compound shows no hydride signal, indicating that the proton is not attached to either metal. However, a multiplet is observed which integrates to one hydrogen at 18.81 ppm, with 7.3 Hz coupling to three hydrogens observed at 1.73 ppm, which appears as a doublet with the same coupling. The low-field resonance is typical of an alkylidene hydrogen with coupling to an adjacent methyl group[25a, b]. Decoupling the rhodium-bound phosphines significantly sharpens the signal at 18.81 ppm, whereas decoupling the molybdenum-bound phosphines has no effect on this signal, indicating that the alkylidene functionality is bound to rhodium. These data suggest, as is observed in the reactions of many vinyl species with protic acids,[25c] that electrophilic attack has occurred on the β-carbon of the vinyl group of **8**, to form a methyl-substituted alkylidene on rhodium, as outlined in Scheme 2.3. The $^{13}C\{^1H\}$ NMR spectrum of **15** displays two carbonyl singlets at 231.7 ppm and 206.7 ppm, attributed to two bridging and two terminal carbonyls, respectively. The low-field carbonyl does not show rhodium coupling, although again, the large half-width of the signal (*ca.* 30 Hz) could mask the small coupling expected for a semibridging carbonyl. All attempts to locate the alkylidene α-carbon in the $^{13}C\{^1H\}$ NMR spectrum were unsuccessful due to low signal intensity, and attempts to obtain an IR spectrum of **15** were unsuccessful due to its facile conversion to a new species, compound **16**. Upon warming to -10 °C, the conversion of **15** to the ethylene adduct, $[RhMo(\eta^2\text{-}C_2H_4)(CO)_4(dppm)_2][BF_4]$ (**16**) is complete. This compound has $^{31}P\{^1H\}$ NMR resonances at 37.2 ppm and 29.9 ppm ($^1J_{Rh\text{-}P}$=131 Hz) for the molybdenum- and rhodium-bound phosphines, respectively. The dppm-methylene pseudoquintet resonance at 3.10 ppm in the ^1H NMR spectrum indicates that the complex has apparent front-back symmetry. The spectrum also displays a signal at 3.58 ppm, which integrates as four hydrogens, the chemical shift of which is consistent with a coordinated olefin. The IR spectrum of this compound shows four bands at 2010, 1967, 1832 and 1813 cm^{-1}, with the low frequency bands suggesting bridging interactions. $^{13}C\{^1H\}$ NMR spectroscopy on this compound displays two resonances in the carbonyl region at 227.3 and 207.3 ppm. The low-field signal is somewhat broad (*ca.* 30 Hz) and could easily mask the small rhodium-coupling of a weak semibridging carbonyl. That the signal at 3.58 ppm in the ^1H NMR spectrum is due to coordinated ethylene was confirmed by carrying out a reaction of $[RhMo(CO)_5(dppm)_2][PF_6]$ with ethylene in the

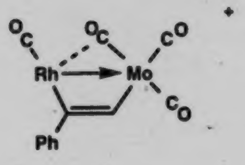
Scheme 2.3. Protonation of Vinyl Complex


HBF$_4$
-80 °C
8
15
Me$_3$NO, C$_2$H$_4$
- CO$_2$
16

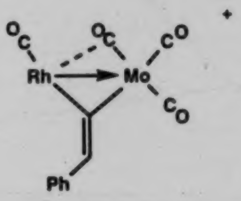
presence of trimethylamine-N-oxide, which produced a small amount of **16** along with various decomposition products. Similar alkylidene-to-olefin rearrangements have been observed previously upon hydride abstraction from [CpRe(NO)(PPh$_3$)(CH$_2$CH$_2$R)],[25b] and upon protonation of the vinyl-containing species, [CpRe(NO)(PPh$_3$)-(CH=CH(CH$_3$)].[25c]

In an attempt to determine the effect of an adjacent third-row metal on the stability of the alkylidene fragment, protonation of the analogous Rh/W vinyl species, [RhW(CH=CH$_2$)(CO)$_4$(dppm)$_2$] (**9**) was carried out. This resulted in the formation of spectroscopically similar alkylidene, [RhW(=CH(CH$_3$))(CO)$_4$(dppm)$_2$][BF$_4$] (**17**) being formed at -80 °C. This product also rearranged to the analogous ethylene-containing species [RhW(η^2-C$_2$H$_4$)(CO)$_4$(dppm)$_2$][BF$_4$] (**18**), but not until approximately 0 °C. The higher temperature required for this transformation indicates that replacement of molybdenum for tungsten has resulted in a slightly more stable alkylidene species, showing a subtle effect due to the presence of an adjacent metal.

Since carbene species are known to undergo coupling reactions with unsaturated substrates,[20] the reactivity of **15** with such species was investigated. It was found however, that the carbene moiety in compound **15** did not react with these substrates. Instead, their addition resulted in displacement of coordinated ethylene from the rearranged isomer, compound **16**. For example, the reaction of **8** with HBF$_4$•(OMe$_2$)$_2$ in the presence of phenylacetylene produces a green phenylacetylene-containing compound, [RhMo(C$_6$H$_5$C$_2$H)(CO)$_4$(dppm)$_2$][BF$_4$], (**17**). The ^{1}H NMR spectrum shows that no coupling of the carbene fragment and phenylacetylene has occurred, in that the only observable hydrogen resonances other than those from the dppm ligands are those due to the phenyl protons of the phenylacetylene moiety, which are shifted upfield slightly from the dppm-phenyl groups due to their presumed proximity to a metal center. The acetylenic hydrogen resonance was not located, presumably being obscured by the dppm-phenyl resonances. An attempt to locate the deuterium resonance derived from monodeutero-phenylacetylene in the ^{2}H NMR also failed, presumably due to H-D exchange between the deuterated compound and the proteo solvent. The $^{13}C\{^{1}H\}$ NMR spectrum displays three singlets due to carbonyls bound to molybdenum, and a doublet of triplets with Rh coupling of 75.4 Hz and ^{31}P coupling of 17.8 Hz, corresponding to a terminally bound carbonyl on Rh. The IR spectrum shows three CO bands at 2007, 1979 and 1843 cm^{-1} with the low-frequency band suggesting a bridging interaction. Again, the rhodium coupling to the presumed bridging carbonyl is likely obscured by the width of the peak (*ca.* 30 Hz). These spectroscopic data do not distinguish between a bridging phenylacetylene (**E**) or a phenylvinylidene ligand (**F**), and location of the phenylacetylene-derived carbons in the $^{13}C\{^{1}H\}$ NMR spectrum in order to differentiate between the two bonding modes was unsuccessful. Coordination of terminal alkynes in a bridging mode, or in a rearranged vinylidene mode is common in binuclear complexes.[24] In both structures shown below, the phenyl group derived from phenylacetylene is shown to be directed away from the molybdenum center due to presumed steric interactions with the molybdenum-bound ligands. The possibility of having the alkyne η^{2}-bound to molybdenum is ruled out, based on the already crowded environment at this metal.



E

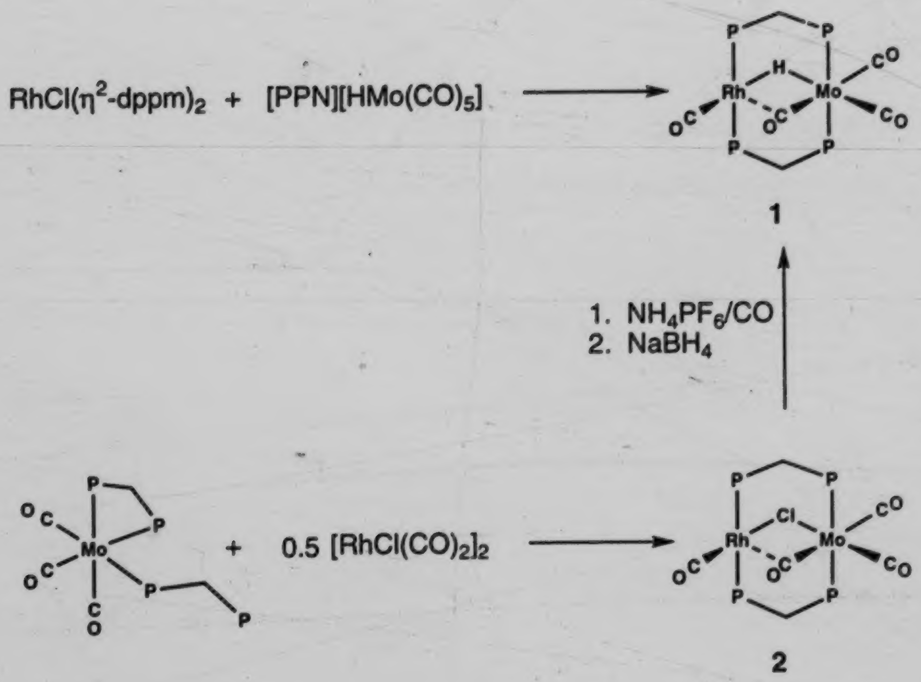


F

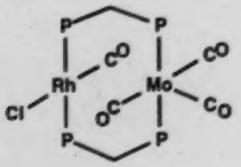
Discussion.

Heterobinuclear complexes containing the Rh/group 6 metal combinations bridged by dppm have been prepared previously in our group, via the reaction of [RhCl(dppm)$_2$] with [PPN][HM(CO)$_5$] (M = Cr, Mo, W), forming the hydrido complexes, [RhM(μ-H)(CO)$_4$(dppm)$_2$].[28] This method provides one route to compound **1**, for which M = Mo. Mixed-metal, dppm-bridged Rh/Group 6 complexes have also been made by others via the reaction of [M(CO)$_3$(η^2-dppm)(η^1-dppm)] with [RhCl(CO)$_2$]$_2$,[12a, b] and this route provides the second class of the two main starting materials used in this study, [RhM(μ-Cl)(CO)$_4$(dppm)$_2$] (M = Mo (**2**), W (**3**)). Both of these reactions result in the "unwinding" of a chelating dppm ligand in the formation of the bimetallic species. This process is often utilized in the preparation of dppm-bridged binuclear complexes, and results from the lower ring strain when the dppm ligand bridges two metals than when it chelates, in which case the resulting four membered ring experiences significant ring strain.[29] These reactions are summarized in Scheme 2.4. Since the second of the above preparations is the more efficient one, in that the starting materials are easy to prepare in large quantities and are stable over long periods, it was the preferred method. In this thesis, compound **1** was prepared from compound **2**,[11] rather than by the alternate route described above. Surprisingly, in the conversion of compound **2** to **1**, compound **2** does not react cleanly with NaBH$_4$; instead compound **1** is prepared by converting **2** into the known pentacarbonyl compound [RhMo(CO)$_5$(dppm)$_2$][PF$_6$], followed by reaction with NaBH$_4$ as shown in Scheme 2.4;[11] a similar effect will be discussed later, in the preparation of the benzyl containing species, [RhMo(CH$_2$Ph)(CO)$_4$(dppm)$_2$] (**12**). Two structures had previously been proposed for the chloro species **2**, as shown in **G**[12a] and **H** below.[12b] Based on our past experience with binuclear, halide-containing complexes, these proposals seemed incorrect. In the first structure **G**, both metals are unsaturated, having

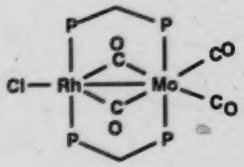
Scheme 2.4


RhCl(η²-dppm)₂ + [PPN][HMo(CO)₅]
1
1. NH₄PF₆/CO
2. NaBH₄
+ 0.5 [RhCl(CO)₂]₂
2

16 valence-electron counts. Although this is common, and in fact expected for rhodium, it is highly unusual for molybdenum. One possible solution to this would be to invoke a dative Rh→Mo bond thereby giving an 18e molybdenum center. In addition, it was puzzling to us that the proposed structure had all terminal carbonyls, in spite of low carbonyl stretching frequencies, which suggested at least a semibridging carbonyl binding mode. The second structure proposed (**H**) is certainly more in keeping with the spectroscopic data and with the electronic requirements of a group 6 metal. In this structure an 18e, *trans*-$Mo(CO)_4P_2$ moiety was proposed in which two of the carbonyls adopt bridging or semibridging interactions with rhodium, giving rise to the two low frequency stretches.



G



H

Although the IR spectrum shows two low-frequency carbonyl bands at 1829 and 1798 cm^{-1}, it was felt that although one of these bands was likely due to a bridging interaction, the other could result from a carbonyl bound terminally on molybdenum; terminal carbonyls in $(PR_3)_2Mo(CO)_4$ complexes often show such low frequency bands (for example, (dppe)$Mo(CO)_4$ and $(dppm)_2Mo(CO)_4$ have low frequency CO bands at 1883 and 1885 cm^{-1}, respectively), and this presumably is why formulation **G** was suggested.[12a] Even with the benefit of the $^{13}C\{^{1}H\}$ NMR spectrum of compound **2**, which shows one terminally-bound carbonyl on rhodium ($^{1}J_{Rh-C}$ = 82.6 Hz), and a broad low-field resonance at 227.4 ppm, the half width (30 Hz) of which could easily mask the rhodium coupling of a semibridging carbonyl, the structure of **2** is not unambiguous. We felt, however, that the most logical structure was one in which rhodium had a square-planar ligand arrangement, much like Vallerino's compound,[30] but having the chloride bridging the rhodium and molybdenum. In this geometry the chloride functions as an anionic four-electron donor, donating a pair of electrons to Rh(+1) and another pair to molybdenum to satisfy their electronic requirements. This is much like the structure proposed for the hydride-bridged compound **1**, and once again demonstrates that halide and hydrido ligands can function as though they have similar electron-donating properties.[31] Our proposal was confirmed by the X-ray structure of compound **2**, shown earlier in Figure 2.1.

A series of alkyl and alkenyl species of the form [RhMoR(CO)$_4$(dppm)$_2$] has been prepared (M = Mo, R = C(CF$_3$)=CHCF$_3$, C(CO$_2$Me)=CHCO$_2$Me, CH=CH$_2$, CH$_3$, η^1-C$_3$H$_5$, CH$_2$Ph, C(O)CH$_2$Ph, and C$_6$H$_5$; M = W, R = CH=CH$_2$). In all cases it was found that the hydrocarbyl fragment is σ-bound to rhodium. When tungsten is substituted for molybdenum, the alkenyl fragment is still σ-bound to rhodium in spite of the stronger carbon-metal bond expected for third-row metals.[23] Presumably, the structure having the organic group on rhodium is favoured by the Rh(I)/M(0) configuration (M = group 6 metal) that results, whereas having the hydrocarbyl fragment bound to the group 6 metal would result in a more unusual Rh(0)/M(I) configuration. Interestingly, these hydrocarbyl Rh/Mo-containing species have structures exactly the same as was incorrectly proposed for the chloro species **2**, shown in **H** above.[12b] This Rh(I)/M(0) arrangement has been observed in other dppm-bridged η^1–hydrocarbyl complexes containing the Rh/Ru[5] and Rh/Os[4a, b] combinations of metals. When both metals are from group 9 (e.g. Rh and Ir) however, both of which have favourable M(I) oxidation states, the σ-bound alkyl fragments are usually bound to the heavier congener, presumably due to a stronger iridium-carbon bond in this case.[3]

The IR spectra of the Rh/Mo complexes described in this chapter all show the presence of terminal and bridging carbonyls, with the $^{13}C\{^1H\}$ NMR spectrum in some cases showing small rhodium-coupling, indicating the carbonyls are interacting with rhodium in a weak semibridging fashion. In many cases however, the large half-width of the low-field carbonyl resonances precluded measuring the small Rh-C coupling constant, so the magnitude of the bridging interaction could not be determined. The $^{13}C\{^1H\}$ NMR spectra of these species typically show two sets of CO resonances, with one at substantially higher field than the other. The high-field resonances are presumably due to terminally-bound carbonyls, whereas the low-field signals are ascribed to semibridging carbonyls. It has been suggested previously that these semibridging interactions serve to alleviate the buildup of excess charge on rhodium, due to the lack of any strongly π-acidic ligands on this metal, combined with the presence of the electron-donating phosphines and σ-hydrocarbyl group, in addition to the Mo$\rightarrow$Rh dative bond, which is required to give rhodium a 16e configuration. These semibridging interactions are apparently typical of dppm-bridged binuclear complexes containing η^1-hydrocarbyl groups.

It was anticipated that these alkyl and alkenyl complexes would provide access to complexes containing two hydrocarbyl or a hydrido and a hydrocarbyl ligand in which the influence of second metal on the migratory insertion and reductive coupling of the organic fragments could be studied. It has been found however that these alkyl and alkenyl complexes are quite unreactive towards a variety of reagents, including CO, H_2O, CH_2N_2, activated alkynes and the powerful electrophile, methyltrifluoromethylsulfonate (methyl triflate). In fact, these complexes have proven to be very stable; they do not react with water and a sample of $[RhMo(CH_3)(CO)_4(dppm)_2]$ (**10**) has displayed minimal decomposition after a period of three years. This low reactivity is in sharp contrast to a variety of isoelectronic alkyl and alkenyl complexes containing Rh and group 8 metals prepared previously in our group. For example, it was found that [RhOs(CH_3)(CO)$_3$-($dppm$)$_2$] readily adds electrophiles such as protic acids and methyl triflate to the osmium center, and in the case of HBF_4 undergoes a series of rearrangements resulting in the reductive elimination of methane.[4a]

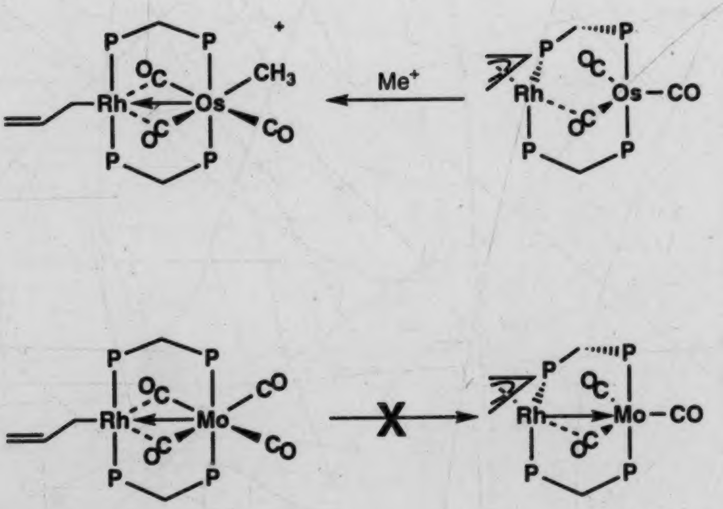
The unreactive nature of the Rh/Mo alkyl-containing species is likely a consequence of several factors. Molybdenum, being electronically saturated, will not react with nucleophiles in an associative manner due to the resulting unfavourable 20-electron configuration, and carbonyl dissociation is unfavourable for these 18e group 6 metals, arguing against a dissociative pathway. Nucleophilic attack on molybdenum-bound carbonyls by reagents such as trimethylamine-N-oxide is disfavoured due to the presence of the two good donor phosphine groups of dppm, consequently attempts to generate vacant coordination sites on molybdenum in this manner were not successful. Electrophilic attack at the molybdenum center is also inhibited by the steric hindrance caused by the presence of the two phosphines and the four carbonyls on this metal. In the Rh/Os case, reaction can occur at the five-coordinate osmium center in an oxidative manner to form cationic species in which the osmium is now six coordinate. This is particularly evident when comparing the reactions of [RhOs(CH_3)(CO)$_3$($dppm$)$_2$] and [RhMo(CH_3)(CO)$_4$($dppm$)$_2$] (**10**) with HBF_4. Addition of HBF_4 to the Rh/Os methyl complex at -80 °C results in an immediate reaction, with the formation of the hydrido-alkyl species [RhOs(H)(CH_3)(CO)$_3$($dppm$)$_2$][BF_4], which subsequently eliminates methane upon warming. However, addition of HBF_4 to the analogous Rh/Mo methyl complex **11** at low temperature, gives no reaction until the solution is warmed to 10 °C at which point reductive elimination of methane occurs. No Rh/Mo hydrido-alkyl species is observed, possibly due to steric congestion causing a fast reductive elimination reaction of methane from a presumed hydrido-methyl intermediate. When the converse reaction is attempted, i.e. the addition of methyl triflate to [RhMo(CO)$_4$(μ-H)(dppm)$_2$] (**2**), the results were much the same, with no immediate reaction observed. After 5 hours, compound **2** was *ca.* 80% consumed, producing the known species [RhMo(CO)$_5$-(dppm)$_2$][OTf], along with various decomposition products. Again, no intermediates were observed during monitoring of this reaction. Although a coordinatively unsaturated metal center adjacent to a saturated metal can increase reactivity at the saturated metal by providing a site for the added ligand to bind to the complex, this appears not be the case with the Rh/Mo system as these unfavorable steric interactions seem to prevent attack of many reagents on the rhodium center as well. The presence of semibridging carbonyls also serves to reduce the nucleophilicity of rhodium, due to the electron withdrawing nature of this interaction, as well as increasing the steric congestion at the rhodium center.

Reaction of [RhMo(CO)$_4$(μ-Cl)(dppm)$_2$] (**2**) with allylmagnesium chloride forms [RhMo(η^1-CH$_2$CH=CH$_2$)(CO)$_4$(dppm)$_2$] (**11**) with the allyl group σ-bound to rhodium. This is in contrast to other results obtained in our group with the Rh/Os system, in which the reaction of [RhOs(CO)$_4$(dppm)$_2$][BF$_4$] with diallylmagnesium yielded [RhOs(η^3-C$_3$H$_5$)(CO)$_3$(dppm)$_2$], having the allyl group η^3-bound to rhodium.[4b] This η^3 coordination mode was facilitated by the rhodium-bound phosphines bending away from the η^3-allyl group, and assuming a cis orientation. In the Rh/Mo case, the phosphines cannot easily assume a cis orientation due to unfavourable interactions with the four carbonyls on molybdenum, consequently the allyl group must bind in an η^1 manner. The effect of increased crowding at the adjacent metal on the binding mode of the allyl group was demonstrated for the complex [RhOs(η^3-C$_3$H$_5$)(CO)$_3$(dppm)$_2$]. Reaction of this η^3-allyl species with methyl triflate occurred at osmium to give [RhOs(η^1-C$_3$H$_5$)(CH$_3$)-(CO)$_3$(dppm)$_2$][OTf], which is isoelectronic with **11**. It is noteworthy that coordination of CH$_3^+$ at osmium resulted in a change in the allyl coordination mode at the other metal.

Presumably the increase of the coordination at osmium from five to six results in the cis-phosphine arrangement at rhodium being unfavourable, resulting in the allyl ligand moving to an η^1-binding mode, as diagrammed below in Scheme 2.5.

Attempts to prepare the benzyl analogue through the addition of a large excess of benzylmagnesium chloride (up to 50 equivalents) to a benzene solution of [RhMoCl-$(CO)_4(dppm)_2$] does not proceed as expected, giving no reaction. However, under an atmosphere of carbon monoxide, with only seven equivalents of the Grignard reagent the reaction goes to completion within several minutes, producing two new compounds-the targeted [RhMo$(CH_2Ph)(CO)_4(dppm)_2$] **(12)** and the acyl analogue, [RhMo-$(C(O)CH_2Ph)(CO)_4(dppm)_2$] **(13)**. If the reaction products are heated to reflux in benzene for several hours, no change in the ratio of the two products is observed. Conversely, if the mixture is placed under an atmosphere of carbon monoxide no conversion of the benzyl species to the phenylacetyl product occurs. This suggests that the products are not interconvertable and are produced by two different pathways. It has previously been shown by Shaw that the addition of NH_4PF_6 to a solution of [RhMo(μ-Cl)$(CO)_4(dppm)_2$] under an atmosphere of carbon monoxide results in the rapid formation of the isolable pentacarbonyl species, [RhMo$(CO)_5(dppm)_2$][PF_6].[12a] Presumably, when [RhMo(μ-Cl)$(CO)_4(dppm)_2$] is placed under an atmosphere of carbon monoxide, an equilibrium is established between it and the pentacarbonyl species, [RhMo$(CO)_5$ $(dppm)_2$][Cl]. We propose that the increase in positive charge and the presence of an extra π-acidic carbonyl ligand increases the electrophilic nature of the rhodium center relative to the neutral chloride species, resulting in rapid formation of the alkylation products. Since [RhMo$(CO)_4$(μ-Cl)$(dppm)_2$] does not appear to react with benzylmagnesium chloride, it seems probable that the reactive species is the

Scheme 2.5

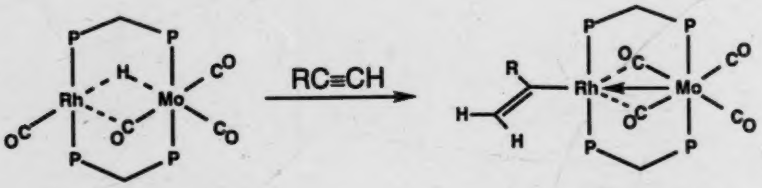

+
Me⁺
Rh
Os
CH3
CO
P
Mo
X

(11)

pentacarbonyl cation and the two products result from competitive attack at a coordinated carbonyl ligand or at the rhodium center.

Alkenyl Complexes from Alkyne Insertion Reactions

A variety of σ-bound alkenyl species have been prepared from the reaction of $[RhMo\text{-}(CO)_4(\mu\text{-}H)(dppm)_2]$ (**1**) with activated alkynes. For example, addition of a large excess of DMAD to **1** yielded a single compound in which insertion of DMAD into the metal-hydride bond occurred to form $[RhMo(MeO_2CC{=}CHCO_2Me)(CO)_4(dppm)_2]$ (**4**); as in all other cases discussed, the organic fragment is σ-bound to the rhodium center. No intermediate containing a hydrido ligand and a coordinated alkyne was observed when NMR spectra were recorded at various intervals during the reaction period. Similar products are obtained when the hydride species is reacted with an excess of the activated alkynes HFB, 3-butyn-2-one, and methyl propiolate. With the latter two unsymmetrical alkynes, the products obtained result from alkyne insertion into the metal-hydride bond, forming a rhodium-carbon bond to the substituted carbon, C(3), of the starting alkyne. On the basis of steric arguments, it would be expected that the alkyne would insert forming a C(4)-Rh bond with the less crowded alkyne carbon. The observed geometry is presumably due to the stronger Rh-C(3) bond that results from the presence of the electron-withdrawing C(O)Me and CO_2Me groups on C(3). This effect has been observed previously, [19a,b, c] and finds an explanation in Bent's rule, which suggests that the electron-withdrawing substituents will increase the carbon s-orbital participation in the Rh-C bond.[19d]



(6) R = C(O)Me

(7) R = CO_2 Me

Alkylidene Complexes from Protonation Reactions

Several methods are known for the preparation of carbene species, including hydride abstraction from alkyl species,[24, 25b] protonation of vinyl complexes[25c] and via the reaction of transition-metal complexes with alkylidene sources such as diazoalkanes.[3c, 34, 35]

Our initial attempts at forming carbenes involved removal of hydride from $[RhMo(CH_2Ph)(CO)_4(dppm)_2]$ with the triphenylmethyl (trityl) cation.[24, 25b] It was found however that instead of removing a hydride, the trityl cation removed the benzyl group, forming $[RhMo(CO)_5(dppm)_2][BF_4]$ along with various decomposition products. This is in contrast with the results obtained for the $CpRe(PPh_3)(NO)(CH_2Ph)$ complex, in which reaction with trityl cation forms the phenyl substituted carbene cation.[24] We assume that in the Rh/Mo case, the bulky dppm-bound phenyl substituents prevent close approach of the large triphenylmethyl cation to the metal-bound benzyl group.

Addition of CH_2N_2 to $[RhOs(CO)_4(dppm)_2][BF_4]$ at low temperature has been shown previously to result in the formation of a species containing a bridging methylene group, $[RhOs(\mu\text{-}CH_2)(CO)_4(dppm)_2][BF_4]$.[33] When the reaction of $[RhMo(CO)_5(dppm)_2][PF_6]$ was carried out with a large excess of diazomethane, polymethylene was produced. In addition, a very small amount of a new compound (<5% by ^{31}P NMR) was observed, although only the starting material could be isolated. The same reaction was carried out in the presence of trimethylamine N-oxide in the hope that CO removal would allow the isolation of a complex containing a methylene unit or coupled methylene fragments. Again, the ^{31}P NMR spectrum showed mostly the starting material and a small amount of a new compound, different from the above mentioned species. The observation of characteristic vinyl resonances in the ^{1}H NMR spectrum of the reaction mixture was encouraging, but the mixture proved to be quite intractable and the new species was not obtained, even with a variety of reaction conditions.

A carbene species could be obtained via protonation of the vinyl complex $[RhMo(CH{=}CH_2)(CO)_4(dppm)_2]$ at -80 °C to give two new compounds, the targeted species, $[RhMo(=CHCH_3)(CO)_4(dppm)_2][BF_4]$ (**15**), and a small amount of the ethylene adduct, $[RhMo(\eta^2\text{-}C_2H_4)(CO)_4(dppm)_2][BF_4]$ (**16**). Above -10 °C conversion of the alkylidene moiety in **15**, via an apparent 1, 2-hydrogen shift to an ethylene ligand in **16**, was complete. Although no intermediate was observed, we suggest that this reaction may occur through β-hydrogen transfer from the alkylidene methyl to rhodium, forming an η^2-vinyl-containing species, followed by reductive elimination of the ethylene moiety to form **16**, as shown previously in Scheme 2.3. η^2-vinyl species are not common, but they have been previously observed and characterized crystallographically.[36] Although rhodium-alkylidene complexes containing heteroatoms in the β-position are well known, those without heteroatoms are quite rare. Of these alkylidene complexes of rhodium, very few have the alkylidene ligand in a terminal position, but are more often found bridging two metals. In the Rh/Mo case it may be that the alkylidene fragment cannot easily move into a bridging position due to unfavourable steric interactions with the dppm phenyl groups; certainly much of the low reactivity of these Rh/Mo species can be attributed to crowding. Similar results have been obtained previously in our group, in which the carbene product $[RhOs(=C(CH_3)_2)(H)(CO)_3(dppm)_2][BF_4]_2$ was formed by protonation of the η^1-isopropenyl precursor. This complex contains a carbene unit terminally bound to rhodium. Although it also decomposed at room temperature, it did not rearrange to an olefin adduct as was observed in **13**; instead, it underwent deprotonation, regenerating the isopropenyl precursor, $[RhOs(CH_3C{=}CH_2)(H)(CO)_3(dppm)_2][BF_4]$.[4b] Attempts to couple the alkylidene unit of **15** with unsaturated organic substrates were unsuccessful. Although the addition of phenylacetylene to the alkylidene species yielded a green phenylacetylene-containing product at room temperature, ^1H NMR spectroscopy showed that coupling of the phenylacetylene and the alkylidene moieties had not occurred; instead the alkyne had merely displaced coordinated ethylene from the rearranged isomer **16**. The resulting product has the phenylacetylene moiety bound either in a parallel-bridging mode, or has isomerized via hydrogen transfer to a vinylidene ligand; both types of products are common in binuclear complexes. Attempts to locate the acetylenic carbon resonances were unsuccessful due to low signal intensity so complete characterization was not possible.

Attempts were made prepare the bis(dimethylphosphino)methane (dmpm) bridged Rh/Mo system in order to increase its reactivity. Dmpm has a much smaller cone angle and is a much better electron donor than dppm.[37] It was anticipated that the use of dmpm as a bridging ligand would have two effects on the reactivity of the bimetallic compound. The smaller size of the ligand should allow for closer approach of reagents to the metal center, and the stronger electron donating ability should increase the system's reactivity towards electrophiles. The approach taken to prepare the bimetallic complex was to first bind the phosphines to molybdenum and then react this molybdenum monomer with a rhodium source, since it was known from previous studies that reaction of dmpm with $[Rh(COD)Cl]_2$ resulted in the formation of binuclear species.[38] Surprisingly, when $Mo(CO)_4(\eta^1\text{-dmpm})_2$ (prepared from the reaction of $Mo(CO)_4(COD)$ with dmpm) was reacted with a variety of rhodium sources the major product obtained was the known compound [$Rh_2Cl_2(CO)_2(dmpm)_2$] along with a small amount of the desired Rh/Mo species. Consequently, this reaction was not pursued further.

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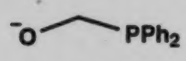
Chapter 3

Preparation of Cyclopentadienyl(alkyl)phosphines and Metallocene Dichloride Derivatives

Introduction

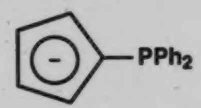
Early-late heterobimetallic (ELHB) complexes are of interest owing to the widely divergent properties of early- and late-transition metals, in the hope that placing two such metals in close proximity may lead to novel reactivities due to cooperative interactions between the two metal types.[1] Although, as will be discussed in Chapter 4, a wide variety of reaction types are available for the preparation of ELHB complexes,[2a-n] one commonly used method involves a multidentate ligand template which is capable of forming strong bonds to both types of metal centers. This eliminates the need for metal-metal bonds to hold the two metal centers in a proximate arrangement,[2e-n] and a variety of suitable ligand types are known, some of which are shown below.[2e-f, j, k]



A

$^{-}CH_2PPh_2$

B



C

Owing to the ubiquitous nature of early-metal cyclopentadienyl and late-metal phosphine chemistry, we have decided to use a ligand similar to the type shown above in **C**. As will be discussed in detail in the next chapter of this thesis, we felt that using the ligand in **C**, in which the PR_2 moiety is bound directly to the cyclopentadienyl ring,[2j-m, 3] would result in geometric constraints on the complex which would lessen the possibility of cooperative behaviour between the two metal centers. It seemed that the introduction of an alkyl spacer between the cyclopentadienyl and phosphino groups might alleviate these restrictions, thus allowing the early-metal substituents to be directed towards the late metal, as has been shown recently in the literature.[2i] Although there has been one report of a metallocene-dichloride-containing ELHB complex, bridged by a ligand like that shown in **C** in which the early-metal substituents were interacting with the late metal; generally, this is not the case, and an X-ray structure of the product showed the system to be quite strained with respect to the phosphorus-late-metal-phosphorus bond angle (*vide infra*).[2j, 4] Accordingly, we have decided to use cyclopentadienylalkylphosphines, containing a "C_1" or "C_2" spacer between the Cp and PR_2 functionalities as a template upon which to prepare our ELHB complexes.

Our strategy for the preparation of the ELHB complexes was to first synthesize metallocene dichlorides, in which the cyclopentadienyl rings are derivatized with an alkyldiphenylphosphino moiety, and then to react these early-metal-containing monomers with a variety of late-metal sources. An important aspect of the study was the elucidation of the effect of the different spacer lengths in the $C_5H_4(CR_2)_nPPh_2$ ligands, where n = 1 or 2, on the structures of the ELHB products, and to correlate this data with the many known ELHB complexes containing the bridging ligand shown in **C** above.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of prepurified argon with standard Schlenk techniques or in a nitrogen-filled Vac Atmospheres glovebox equipped with an HE-493 dri-train. Solvents were dried and distilled under nitrogen immediately before use. Sodium benzophenone was used as the drying agent except with CH_2Cl_2 which was distilled from P_2O_5. Group IV metal salts and diphenylphosphine were purchased from Strem or Aldrich. Diphenylphosphine and $TiCl_4$ were used as received and $ZrCl_4$ was sublimed immediately before use. Spiro[2.4]-

hepta-4,6-diene[5] and fulvene[6] were prepared via literature methods. $KPPh_2$ was prepared by the reaction of $HPPh_2$ with excess KH in THF solution and $LiPPh_2$ was prepared via the reaction of $HPPh_2$ with one equivalent of n-BuLi (2.5 M in hexanes) in THF. Dimethylphosphine[7] was prepared via the reaction of tetramethyldiphosphine disulfide with $LiAlH_4$. The product was distilled from the reaction vessel directly into a flask containing *ca.* 1 mole equivalent of n-BuLi in 50 mL of n-pentane that had been cooled to -80 °C, and the resulting $LiPMe_2$ was collected on a glass frit.

The ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AM-400 spectrometer operating at 400.1, 162.0 and 100.6 MHz for the respective nuclei. The internal deuterated solvent served as a lock for the spectrometer. Elemental analyses were performed by the microanalytical service within the department. Spectroscopic data for all compounds are given in Table 3.1.

Preparation of Compounds. (a) $K[C_5H_4CH_2CH_2PPh_2]$ (20). A solution of 8.9 g (0.0397 mol) of $KPPh_2$ in 220 mL of THF was added to 4.5 mL (0.0439 mol) of spiro[2.4]hepta-4,6-diene in 450 mL of THF at -80°C. The solution was warmed to room temperature and stirred for 3 h, during which time a white crystalline solid was produced. The solution was concentrated in vacuo to ca. 2/3 of the original volume and the precipitate was collected on a glass frit. Yield 9.0g, 72% based on $KPPh_2$. The compound is obtained spectroscopically pure, but elemental analyses could not obtained due to its highly air sensitive nature.

(b) $Li[C_5H_4CH_2CH_2PMe_2]$ (21). A suspension of 1.694 g (0.0250 mol) of $LiPMe_2$ in 10 mL of n-pentane was cooled to - 80 °C and then 40 mL of THF was added. This solution was added to 2.8 mL (0.0274 mol) of spiro[2.4]hepta-4,6-diene in 20 mL of THF at -80 °C, and then the solution was warmed to room temperature. After stirring for 3 h, the solvent was removed in vacuo and then the white solid was triturated in 50 mL of

Table 3.1. Spectroscopic Data for Compounds[a]

	NMR[b]	
compound:	$\delta(^{31}P\{^1H\})$ (ppm)	$\delta(^1H)$ (ppm)
$K[C_5H_4CH_2CH_2PPh_2]$ **(20)**[c]	-16.1(s)	2.82(dt, 2H, $^3J_{HH}$= 7.0 Hz, J_{HP}= 11.1 Hz, $C_5H_4\mathit{CH_2CH_2}PPh_2$) 2.29(t, 2H, $^3J_{HH}$= 7.0 Hz, $C_5H_4\mathit{CH_2CH_2}PPh_2$) 5.40(m, 2H, $C_5\mathit{H_4}CH_2CH_2PPh_2$) 5.43(m, 2H, $C_5\mathit{H_4}CH_2CH_2PPh_2$)
$Li[C_5H_4CH_2CH_2PMe_2]$ **(21)**[c]	-55.9(s)	1.61(dt, 2H, $^3J_{HH}$= 7.8 Hz, J_{HP}= 1.2 Hz, $C_5H_4\mathit{CH_2CH_2}PMe_2$) 2.61(dt, 2H, $^3J_{HH}$= 7.8Hz, J_{HP}= 10.3 Hz, $C_5H_4\mathit{CH_2CH_2}PMe_2$) 5.48(m, 2H, $C_5\mathit{H_4}CH_2CH_2PMe_2$) 5.53(m, 2H, $C_5\mathit{H_4}CH_2CH_2PMe_2$)
$K[C_5H_4CH_2PPh_2]$ **(22)**[c]	-16.3(s)	3.41(s, br, 2H, $C_5H_4\mathit{CH_2}PPh_2$) 5.37(s, br, 4H, $C_5\mathit{H_4}CH_2PPh_2$)
$[Me_2C(C_5H_3{=}CMe_2)_2]$ **(23)**[d]		1.49(s, 6H, $C\mathit{Me_2}$) 2.16(s, 6H, $=C\mathit{Me}$) 2.17(s, 6H, $=C\mathit{Me}$) 6.22(m, 2H, $=C\mathit{H}$) 6.42(m, 2H, $=C\mathit{H}$) 6.49(m, 2H, $=C\mathit{H}$)
$[Li]_2[Me_2C(C_5H_3CMe_2PPh_2)_2]$ **(24)**[c]	20.2(s)	1.30(d, 12H, $^3J_{HP}$= 11.8 Hz, $C\mathit{Me_2}PPh_2$) 1.61(s, 6H, $\mathit{Me_2}C(C_5H_3CMe_2PPh_2)_2$) 5.58(m, 2H,$C_5\mathit{H_3}$) 5.65(m, 2H, $C_5\mathit{H_3}$) 5.77(m, 2H, $C_5\mathit{H_3}$)
$[(\eta^5\text{-}C_5H_4CH_2CH_2PPh_2)_2TiCl_2]$ **(25)**	-16.5(s)	2.36(t, 4H, $\mathit{CH_2CH_2}PPh_2$) 2.81(dt, 4H, J_{HP}= 9.0 Hz, J_{HH}= 7.5 Hz, $\mathit{CH_2CH_2}PPh_2$) 6.26(m, 4H, $C_5\mathit{H_4}$) 6.33(m, 4H, $C_5\mathit{H_4}$)

Table 3.1 (cont.)

$[(\eta^5\text{-}C_5H_4CH_2CH_2PPh_2)_2ZrCl_2]$ (26)	-16.5(s)	2.33(t, 4H, J_{HH}= 8.0 Hz, $CH_2CH_2PPh_2$) 2.73(dt, 4H, J_{HP}= 9.1Hz, J_{HH}= 8.0 Hz, $CH_2CH_2PPh_2$) 6.18(m, 4H, C_5H_4) 6.25(m, 4H, C_5H_4)
$[(\eta^5\text{-}C_5H_4CH_2PPh_2)_2TiCl_2]$ (27)	-9.6(s)	3.51(s, br, 4H, CH_2PPh_2) 6.00(m, 4H, C_5H_4) 6.25(m, 4H, C_5H_4)
$[(\eta^5\text{-}C_5H_4CH_2PPh_2)_2ZrCl_2]$ (28)	-9.7(s)	3.41(s, br, 4H, CH_2PPh_2) 5.94(m, 4H, C_5H_4) 6.17(m, 4H, C_5H_4)
$[Me_2C(C_5H_3CMe_2PPh_2)_2ZrCl_2$ (29)	32.7(s)	1.48(d, 6H, $^3J_{HP}$= 13.0 Hz, CMe_2PPh_2) 1.58(s, 6H, $Me_2C(C_5H_3CMe_2PPh_2)_2$ 1.75(d, 6H, $^3J_{HP}$= 16.2 Hz, CMe_2PPh_2) 5.07(m, 2H, C_5H_3) 5.48(m, 2H, C_5H_3) 5.99(m, 2H, C_5H_3)

[a] Abbreviations used: for NMR (s) singlet, (d) doublet, (dt) doublet of triplets, (m) multiplet, (dd) doublet of doublets, (br) broad; [b] NMR spectra recorded in CD_2Cl_2 unless otherwise stated; [c] NMR spectra recorded in THF-D8; [d] NMR spectra recorded in $CDCl_3$; phosphorus-bound phenyl groups omitted.

n-pentane, followed by collection on a glass frit and washing with 3×10 mL of n-pentane. The solid was dried in vacuo to give 2.792 g (70%) of a spectroscopically pure product. Elemental analyses were not obtained due to the highly air sensitive nature of the compound.

(c) $K[C_5H_4CH_2PPh_2]$ (22). 16.0 g (0.0713 mol) of $KPPh_2$ in a mixture of 100 mL THF and 300 mL of Et_2O was added to a solution of 4.45 g (0.0570 mol) of fulvene in 300 mL of Et_2O at -80°C, resulting in the immediate formation of an off-white precipitate. The mixture was warmed to room temperature with vigorous stirring and then the solid was collected on a frit. Yield 13.6 g, 63 % based on $KPPh_2$. The compound is obtained spectroscopically pure, but elemental analyses were not obtained due to its highly air sensitive nature.

(d) $[Me_2C((C_5H_3{=}C(CH_3)_2)_2]$ (23). This compound was prepared as previously reported, with minor modifications.[8] 4.36 mL (0.0522 mol) of pyrrolidine were added to 1.853 g (0.0109 mol) of $(C_5H_4)_2CMe_2$ and 1.6 mL (0.0218 mol) of acetone in 26 mL of a 10:1 mixture of $MeOH{:}Et_2O$ at 5 °C. The solution was stirred at room temperature for 16.5 h and then 3.2 mL (0.0559 mol) of acetic acid was added in at - 10 °C. 30 mL of water and 30 mL of Et_2O were added in air and the organic layer was removed. The aqueous layer was washed with 3×20 mL of Et_2O, then the organic portions were combined and washed with 3×20 mL of water, 1×20 mL brine and then dried over Na_2SO_4 and molecular sieves. The solvent was removed under reduced pressure, and the crude yellow oil eluted through a filter containing *ca.* 8 cm × 8 cm silica. The solvent was removed under reduced pressure yielding 2.243 g, 82 % of a yellow oil.

(e) $Li_2[Me_2C(C_5H_3C(CH_3)_2PPh_2)_2]$ (24). 2.20 g (8.72 mmol) of fulvene **23** in 50 mL of THF was added to a solution of $LiPPh_2$ (17.2 mmol) in 80 mL of THF at -80 °C over 5 min. The solution was warmed to room temperature and stirred for 16 h, and then the solvent was removed in vacuo. The orange foamy residue was triturated with 100 mL of n-pentane until a powdery off-white solid was obtained, which was collected on a glass frit and washed with 3×20 mL of n-pentane, followed by drying in vacuo. Yield 7.69 g, 70 % based on $LiPPh_2$. The compound was obtained spectroscopically pure, but elemental analyses could not be obtained due to the highly air sensitive nature of the compound.

(f) $[(\eta^5\text{-}C_5H_4CH_2CH_2PPh_2)_2TiCl_2]$ (25). Method 1: A solution of 0.866g (2.593 mmol) of $TiCl_4(THF)_2$ in 50 mL of THF was added dropwise to 2.246 g of $K[C_5H_4CH_2CH_2PPh_2]$ (**20**) in 110mL of THF over 2 hours. After stirring overnight, a red solution had formed (if the solution is brown at this point, conc. HCl can be added dropwise until a red solution is formed), and the solvent was removed in vacuo. The residue was extracted with 3×20 mL of toluene and the extracts filtered through Celite to remove KCl and polymeric materials, and then the solvent was removed in vacuo. The red residue was triturated with three 10 mL portions of Et_2O yielding 520 mg of a red powder. Yield 30%. Anal. Calcd. for $C_{36}H_{32}P_2Cl_2Ti$: C, 67.77 %; H, 5.39 %. Found: C, 67.60 %; H, 5.38 %.

Method 2: A solution of 0.568 g (1.63 mmol) of $TiCl_3(THF)_3$ in 60 mL of THF was added to 1.100 g (3.47 mmol) of $K[C_5H_4CH_2CH_2PPh_2]$ (**20**) in 120 mL of THF at -80°C over 30 min. The solution was warmed to room temperature and stirred for 19 h, during which time the color changed to dark green. The flask was opened to the air and *ca.* 3.5 mL conc. HCl was added resulting in a color change to red over 5 minutes. The solution was cooled to -40 °C and then 2 mL of pyridine was added to the solution and then was warmed to room temperature. After stirring for several minutes at room temperature, the solvent was removed in vacuo. The residue was extracted with 4×10 mL of toluene, then the extracts were filtered through Celite to remove KCl and polymeric materials, and the solvent removed in vacuo. The red residue was triturated in Et_2O (4×15 mL) resulting in the formation of a red powder. Yield 628 mg, 57%. The product is spectroscopically identical to that obtained by Method 1.

(g) $[(\eta^5\text{-}C_5H_4CH_2CH_2PPh_2)_2ZrCl_2]$ (26). 815 mg (2.576 mmol) of $K[C_5H_4CH_2CH_2PPh_2]$ **(20)** in 20 mL of toluene was added to 300 mg (1.287 mmol) of $ZrCl_4$ in 20 mL toluene at -80°C. The solution was warmed slowly to room temperature and stirred for 18 h. The solvent was removed in vacuo then the residue dissolved in 40 mL of CH_2Cl_2 and filtered through Celite. If the filtrate is yellow, then a small amount (*ca.* 100 mg) of activated carbon may be added, followed by stirring for 5 min and filtration through Celite to give a colorless solution. Alternatively, the yellow impurity may be precipitated by the addition of n-pentane to a CH_2Cl_2 solution of the compound at 0 °C, followed by solvent removal via cannula. The solvent from the filtrate was removed in vacuo and the colorless residue recrystallized by dissolving in 5 mL of CH_2Cl_2, cooling to -20°C, and slowly adding 30 mL of n-pentane. The solvent was removed via cannula and the white microcrystalline solid washed with 3×10 mL of n-pentane and then dried in vacuo. Crystalline material may be obtained by adding n-pentane to a CH_2Cl_2 solution of the compound at 0 °C until the solution becomes slightly turbid, followed by cooling to -20 °C for 48 h. Yield 415 mg, 45 %. Anal. Calcd. for $C_{38}H_{36}P_2Cl_2Zr$: C, 63.68%; H, 5.06%. Found: C, 63.45%; H, 5.01%.

(h) $[(\eta^5\text{-}C_5H_4CH_2PPh_2)_2TiCl_2]$ (27). 286 mg (0.823 mmol) of $TiCl_3(THF)_3$ in 30 mL of THF was added to 548 mg (1.81 mmol) $K[C_5H_4CH_2PPh_2]$ **(22)** in 60 mL of THF at -80°C over 30 min. The solution was warmed to room temperature and stirred for 18 h. 25 drops of conc. HCl was added in air to the green solution resulting in an immediate color change to red. After stirring for 2 min the solvent was removed in vacuo and the red residue extracted with 4×10 mL of toluene. The extracts were filtered through

Celite and the solvent removed in vacuo. The red residue was triturated with n-pentane (3×10 mL) until a red powder was obtained which was then dried in vacuo. Yield 290 mg, 55 %. Anal. Calcd. for $C_{36}H_{32}P_2Cl_2Ti$: C, 67.00 %; H, 5.00 %. Found: C, 66.53 %; H, 5.23 %.

(i) $[(\eta^5\text{-}C_5H_4CH_2PPh_2)_2ZrCl_2]$ (28). A suspension of 368 mg (1.22 mmol) of $K[C_5H_4CH_2PPh_2]$ (**22**) in 15 mL of toluene was added to a suspension of 136 mg (0.583 mmol) of $ZrCl_4$ in 15 mL of toluene at -80°C over 5 min. The suspension was warmed slowly to room temperature and stirred for a total of 18 h. The solvent was removed in vacuo and the residue dissolved in 20 mL of CH_2Cl_2, followed by filtration through Celite. The solvent was removed in vacuo and the yellow oily solid redissolved in 3 mL of CH_2Cl_2 and cooled to -10 °C. 30 mL of n-pentane was added resulting in the formation of an oily yellow solid and milky white suspension. The suspension was removed via cannula and the solvent volume reduced to 1/2 in vacuo and cooled to -20°C. 10 mL of n-pentane was added and the mixture was stirred at -20°C for 30 min. The solvent was removed via cannula and the white solid washed with 2×10 mL n-pentane and dried in vacuo. Yield 107 mg of an analytically pure product. The oily solid was triturated in 3×10 mL n-pentane and dried in vacuo to give 49 mg of a spectroscopically pure product. Total yield 156 mg, 40%. Anal. Calcd. for $C_{36}H_{32}P_2Cl_2Zr$: C, 62.78%; H, 4.68%. Found: C, 62.62%; H, 4.66%.

(j) $[Me_2C(C_5H_3C(CH_3)_2PPh_2)_2ZrCl_2]$ (29). 563 mg (0.884 mmol) of $[Li]_2$-$[Me_2C(C_5H_3C(CH_3)_2PPh_2)_2]$ (**24**) in 25 mL of toluene was added to 200 mg (0.858 mmol) of $ZrCl_4$ in 15 mL of toluene at -80 °C over 5 min. The solution was warmed slowly to room temperature and stirred for 16.5 h. The solvent was removed in vacuo and then 20 mL of CH_2Cl_2 was added, and the yellow solution was filtered through Celite. The solvent was removed in vacuo and the residue was recrystallized by dissolving in 3 mL of

CH_2Cl_2, cooling to - 15 °C, and then adding 20 mL n-pentane resulting in the formation of a yellow-brown solid. The solution was filtered through Celite at - 15 °C, and then the solvent was removed in vacuo yielding a bright yellow solid. Trituration of this solid with 3×10 mL of n-pentane gave a bright yellow powdery solid. Yield 269 mg, 40%. Anal. Calcd. for $C_{43}H_{44}P_2Cl_2Zr$: C, 65.80%; H, 5.65%. Found: C, 65.17%, H, 5.65%. Repeated attempts to obtain satisfactory carbon analyses were unsuccessful.

X-ray Data Collection

X-ray data collection and structure solution were carried out be Dr. R. McDonald. A colorless crystal of $[(\eta^5\text{-}C_5H_4CH_2CH_2PPh_2)_2ZrCl_2]$ **(26)** was obtained by slow cooling of a CH_2Cl_2/n-pentane solution to -20 °C. See Table 3.2 for experimental details. The structures were solved by direct methods, using the SHELXS–86[9] software package.

Results and Compound Characterization.

Preparation of Compounds.

Cyclopentadienyl rings with a large variety of functional groups have been reported in the literature.[10] Many early methods for the derivatization of Cp rings involved the use of the reactions of Cp anions with alkyl halides.[11] However, in recent years many new synthetic methods have been developed owing to the poor nucleophilicity of the Cp^- anion. Particularily popular is the use of nucleophilic additions to five-membered rings containing Cp precursors, which afford Cp anions directly,[12] some examples of which are shown in Scheme 3.1 below.

Our initial attempts to prepare Cp(alkyl)phosphines were via the halide-displacement reactions mentioned above because previous literature had reported the successful preparation of cyclopentadienylethyldiphenylphosphine from the reaction of $ClCH_2CH_2PPh_2$ with Cp^-.[2h] We have attempted this procedure and found it to be

Table 3.2. Crystallographic Experimental Details for [η^5-$C_5H_4CH_2CH_2PPh_2)_2ZrCl_2$]**(26)**

A. Crystal Data	
formula	$C_{38}H_{36}Cl_2P_2Zr$
formula weight	716.73
crystal dimensions (mm)	0.70 × 0.50 × 0.29
crystal system	monoclinic
space group	*I*2/*a* (a nonstandard setting of *C*2/*c* [No. 15])
unit cell parameters[a]	
a (Å)	26.974 (3)
b (Å)	6.4587 (9)
c (Å)	20.671 (2)
β (deg)	105.598 (8)
V (Å^3)	3468.5 (7)
Z	4
ρ_{calcd} (g cm^{-3})	1.373
μ (mm^{-1})	0.589
B. Data Collection and Refinement Conditions	
diffractometer	Siemens P4/RA[b]
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	–60
scan type	θ–2θ
data collection 2θ limit (deg)	50.0
total data collected	6236 ($-32 \le h \le 32$, $-7 \le k \le 7$, $-24 \le l \le 24$)[c]
independent reflections	3053
number of observations (*NO*)	2707 ($F_o^2 \ge 2\sigma(F_o^2)$)
structure solution method	direct methods (*SHELXS–86*[d])
refinement method	full-matrix least-squares on F^2 (*SHELXL–93*[e])
absorption correction method	semiempirical (ψ scans)
range of transmission factors	0.8765–0.8039
data/restraints/parameters	3053 [$F_o^2 \ge -3\sigma(F_o^2)$] / 0 / 195
goodness-of-fit (*S*)[f]	1.077 [$F_o^2 \ge -3\sigma(F_o^2)$]
final *R* indices[g]	
$F_o^2 > 2\sigma(F_o^2)$	**R_1 = 0.0279**, wR_2 = 0.0648
all data	R_1 = 0.0336, **wR_2 = 0.0676**
largest difference peak and hole	0.378 and –0.240 e Å^{-3}

[a]Obtained from least-squares refinement of 40 reflections with $25.4° < 2\theta < 28.0°$.

[b]Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Siemens.

[c]Data were collected from Friedel-opposite quadrants of reciprocal space with indices of the form $(+h\ -k\ \pm l)$ and $(-h\ +k\ \pm l)$.

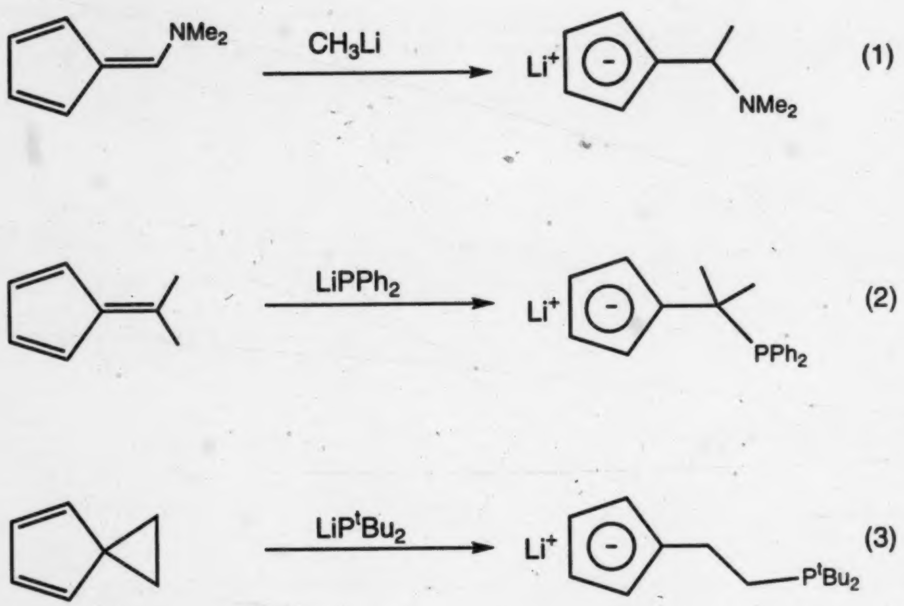
[d]Sheldrick, G. M. *Acta Crystallogr.* **1990,** *A46*, 467–473.

[e]Sheldrick, G. M. *SHELXL-93*. Program for crystal structure determination. University of Göttingen, Germany, 1993. Refinement on F_o^2 for all reflections (all of these having $F_o^2 \geq -3\sigma(F_o^2)$). Weighted *R*-factors wR_2 and all goodness of fit *S* are based on F_o^2; conventional *R*-factors R_1 are based on F_o, with F_o set to zero for negative F_o^2. The observed criterion of $F_o^2 > 2\sigma(F_o^2)$ is used only for calculating R_1, and is not relevant to the choice of reflections for refinement. *R*-factors based on F_o^2 are statistically about twice as large as those based on F_o, and *R*-factors based on ALL data will be even larger.

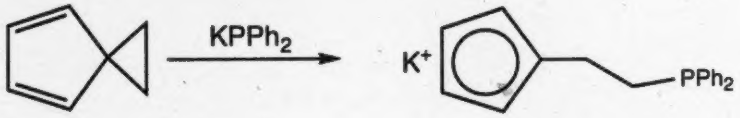
[f]$S = [\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0342P)^2 + 1.9425P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[g]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Scheme 3.1


NMe2
CH3Li
Li+
NMe2
(1)
LiPPh2
Li+
PPh2
(2)
LiPtBu2
Li+
PtBu2
(3)

unsatisfactory. Our current preparation is a modification of a method used later by another group, in which they reported that the targeted ligand may be obtained via the reaction of lithium diphenylphosphide with spiro[2,4]hepta-4,6-diene, followed by hydrolysis and then purification via chromatography.[12b] We have found that the ligand may be obtained more conveniently as a spectroscopically pure crystalline solid by the reaction of $KPPh_2$, instead of the lithium salt, with spiro[2,4]hepta-4,6-diene, as shown below, and may be used directly without further purification.



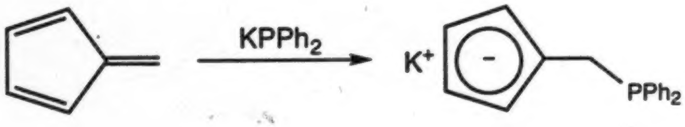
72%

20

$K[C_5H_4CH_2CH_2PPh_2]$ (**20**) has a $^{31}P\{^1H\}$ NMR chemical shift of -16.1 ppm, and the ^1H NMR spectrum shows methylene signals at 2.20 as a triplet ($^3J_{HH}$ = 7.0 Hz) and 2.82 ppm as a doublet of triplets (J_{HH} = 7.0 Hz, J_{HP} = 11.1 Hz). The cyclopentadienyl region of the ^1H NMR spectrum displays two AA'BB' multiplets at 5.40 and 5.43 ppm, the pattern of which appears to be typical of these compounds. In a similar reaction, the dimethylphosphino derivative $Li[C_5H_4CH_2CH_2PMe_2]$ (**21**) is obtained, which displays a singlet in the $^{31}P\{^1H\}$ NMR spectrum, at -55.9 ppm, and methylene resonances in the ^1H NMR spectrum at 1.61 and 2.61 ppm, with the Cp hydrogen signals at 5.48 and 5.53 ppm.

The analogous "C_1" ligand, with a 1-carbon spacer between the cyclopentadienyl and phosphine units, $K[C_5H_4CH_2PPh_2]$ (**22**) is obtained via addition of the diphenylphosphide anion to a solution of fulvene at low temperature, as shown below. $^{31}P\{^1H\}$ NMR spectroscopy on this compound shows a singlet at -16.3 ppm. The ^1H

NMR spectrum of this ligand has a methylene resonance at 3.41 ppm and in this case, the cyclopentadienyl hydrogens are apparently coincidently degenerate, resonating at 5.37 ppm.



63%

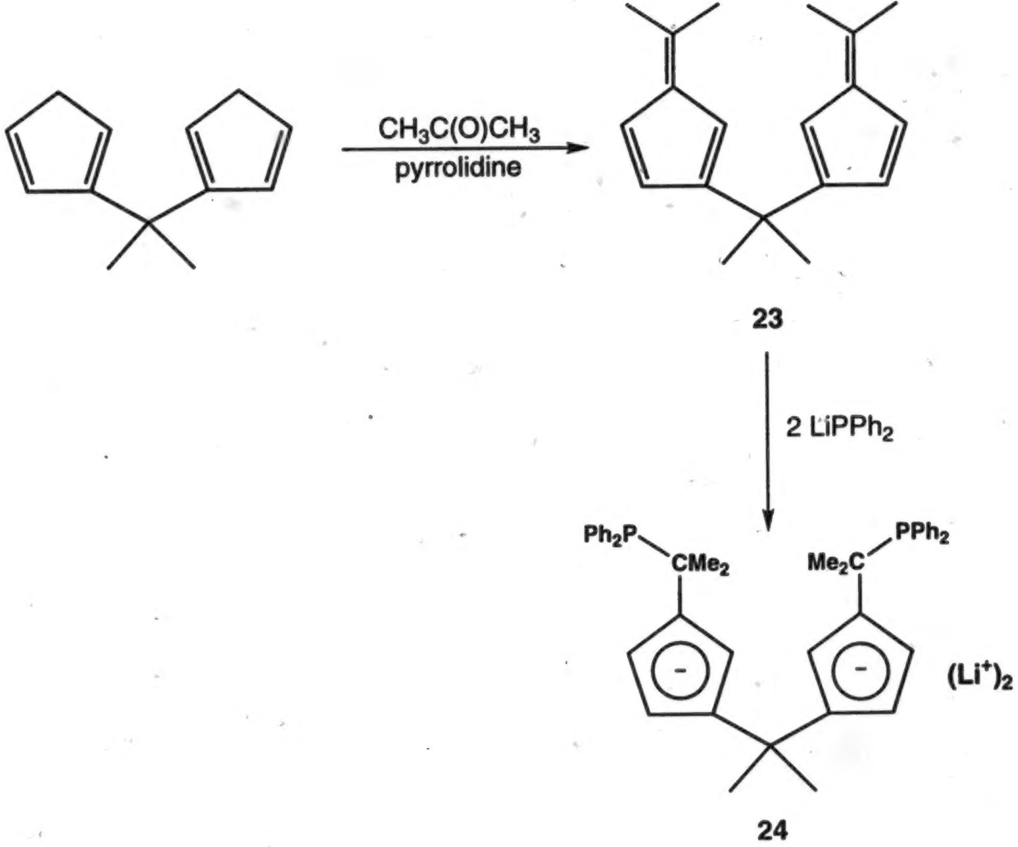
22

Another "C_1" ligand, in which each Cp ring is linked to the phosphine moiety by a $C(CH_3)_2$ spacer group, and in which the Cp rings are also connected to each other by a $C(CH_3)_2$ linker, is obtained by addition of lithium diphenylphosphide to the fulvene shown in Scheme 3.2 below. The presence of alkyl substituents on the spacer carbon between the Cp and PPh_2 groups results in a large change in the ^{31}P NMR chemical shift, when compared to $K[C_5H_4CH_2PPh_2]$ (**22**), with the resonance for the two equivalent phosphines appearing as a singlet at 20.2 ppm. The ^1H NMR spectrum shows a doublet for the methyls bound to the spacer-carbon with phosphorus coupling of 11.8 Hz, and this coupling allows for the differentiation of this signal and that of the methyls bound to the linker carbon (linking the two Cp groups), which appears as a singlet at 1.61 ppm. Three separate multiplets are observed for the cyclopentadienyl hydrogens, at 5.58, 5.65 and 5.57 ppm.

Preparation of Metallocene Dichlorides

Our strategy for the preparation of ELHB complexes was to first complex the cyclopentadienyl unit of the heterodifunctional ligands to an early metal, followed by reaction of these metallocene dichloride derivatives with late-metal sources. $[(\eta^5\text{-}C_5H_4CH_2CH_2)_2TiCl_2]$ (**25**) was prepared initially by the reaction of

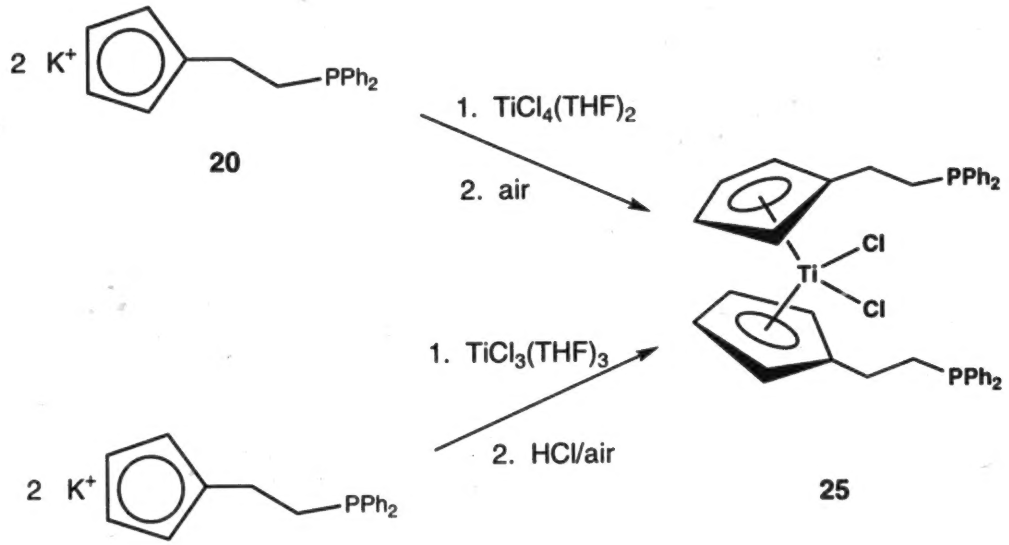
Scheme 3.2



$CH_3C(O)CH_3$
pyrrolidine
23
2 $LiPPh_2$
Ph_2P
CMe_2
Me_2C
PPh_2
-
-
$(Li^+)_2$
24

$K[C_5H_4CH_2CH_2PPh_2]$ (**20**) with $TiCl_4(THF)_2$. This reaction proceeds with concomitant reduction of Ti(IV) to Ti(III), as evidenced by the formation of a dark green solution, the color of which is typical for "Cp_2TiCl" species. It was found that pure **25** could be obtained, albeit in low yield, by air oxidation of the green solutions, followed by subsequent workup, as shown in Scheme 3.3. Alternatively, compound **25** may be obtained in higher yield via the reaction of $K[C_5H_4CH_2CH_2PPh_2]$ (**20**) with $TiCl_3(THF)_3$, followed by oxidation with HCl. Although an analytically pure product may be obtained via this method, signals in the ^1H and ^{31}P NMR spectra of the product are often broadened slightly, presumably due to the presence of small amounts of paramagnetic Ti(III)-containing impurities. The $^{31}P\{^1H\}$ NMR spectrum of compound **25** displays a singlet at -16.5 ppm, and the similarity of this signal to that of the free ligand (δ = -16.1 ppm) suggests that the phosphorus is not coordinated to the titanium center. The ^1H NMR spectrum of this compound is similar to that of the free ligand, with the two methylene resonances appearing as a triplet at 2.36 ppm, with 7.5 Hz coupling to a doublet of triplets at 2.81 ppm (the doublet due to phosphorus coupling of 9.0 Hz). The Cp hydrogen signals are shifted to lower-field from those of the free ligand, with multiplets at 6.26 and 6.33 ppm. The downfield shift is presumably due to a decrease in electron-density around the ligand upon coordination to the metal, and was observed in most of the metallocene dichlorides prepared in this work. The zirconocene dichloride derivative, $[(\eta^5\text{-}C_5H_4CH_2CH_2PPh_2)_2ZrCl_2]$ (**26**), may be prepared via the reaction of $K[C_5H_4CH_2CH_2PPh_2]$ (**20**) with either $ZrCl_4$ or $ZrCl_4(THF)_2$ and has remarkably similar spectroscopic properties to compound **25**, with an identical ^{31}P NMR chemical shift of -16.5 ppm, and very similar cyclopentadienyl hydrogen resonances appearing in the ^1H NMR spectrum at 6.18 and 6.25 ppm. Single crystals of compound **26**, suitable for X-ray analysis, were obtained by slowly cooling a CH_2Cl_2/n-pentane solution of the

Scheme 3.3 Preparation of $[(\eta^5\text{-}C_5H_4CH_2CH_2PPh_2)_2TiCl_2]$ (25)


2 K⁺
PPh₂
20
1. TiCl₄(THF)₂
2. air
1. TiCl₃(THF)₃
2. HCl/air
2 K⁺
PPh₂
PPh₂
Cl
Ti
Cl
PPh₂
25

complex. The structure of compound **26** consists of a typical pseudotetrahedral ligand arrangement around zirconium, as shown in Figures 3.1 and 3.2. See Table 3.3 for selected bond lengths and angles. The Zr-Cl bond lengths and Cl-Zr-Cl' bond angles of 2.4448(6) Å and 99.69 Å, respectively (see Table 3.3 for structural parameters), are typical of zirconocene-type compounds.[13] Although one might have anticipated that the bulky Cp substituents would be staggered with respect to each other, they are twisted only slightly from an eclipsed conformation, where the C(2)-C(10)-C(10)'-C(2)' torsion angle is 25.0°, and the substituents essentially bisect the Cl-Zr-Cl' angle. However, the alkylphosphino arms are directed away from each other, as would be expected based on steric considerations (see Figure 3.2). In this position, however, they minimize repulsions between each other by occupying the carbons that are furthest from each other on opposite Cp rings, and which also point away from the center of mass of the molecule. This is exactly the orientation desired for using this $Cp_2^xZrCl_2$ moiety as a bidentate metalloligand, except that the phosphines are directed in essentially the opposite direction (up and down in Figures 3.1 and 3.2). The crystal structure of this complex differs substantially from the structure of an analogous compound, *rac*-$[C_5H_4CH(CH_3)PPh_2)_2$-$ZrCl_2]$, shown in **A** below, mainly with respect to the orientation of the alkyldiphenylphosphino arms.[2i] In compound **A**, these substituents are oriented with a C(6)-Cp(c)-Cp(c)'-C(6)' dihedral angle of 178.6°, as shown below (where C(6) and C(6)' are the spacer carbons), so they have a totally staggered arrangement and are also oriented at *ca.* 90° to the Cl-Zr-Cl bisector. This means that in order for compound **A** to act as a chelating metalloligand on a late-transition metal, with the Zr-bound halides directed towards the late metal (which is ideal for the transfer of substituents between metal centers), both Cp rings must rotate by *ca.* 90°, in forming a bimetallic complex.

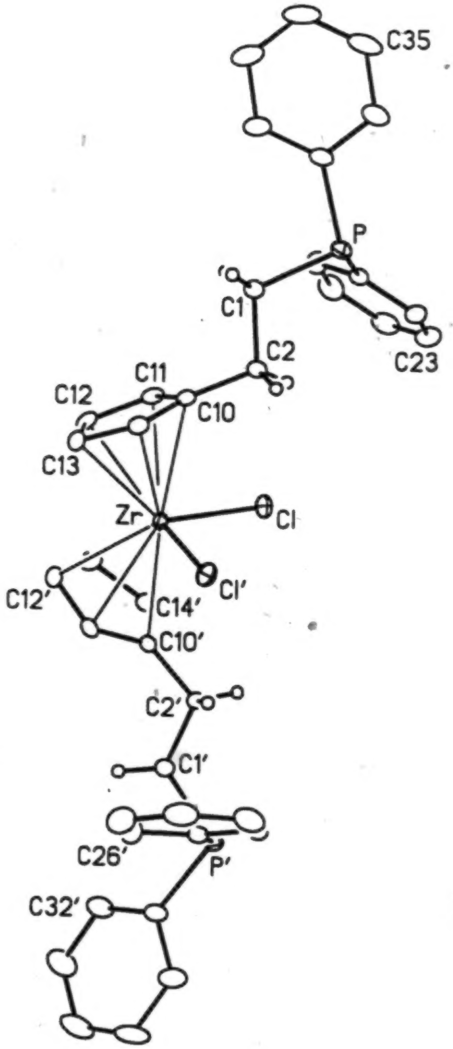

C35
P
C1
C2
C23
C11
C12
C10
C13
Zr
Cl
Cl'
C12'
C14'
C10'
C2'
C1'
C26'
P'
C32'

Figure 3.1. Perspective view of the $[(\eta^5\text{–}C_5H_4CH_2CH_2PPh_2)_2ZrCl_2]$ **(26)** molecule showing the atom labelling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters for the methylene groups, and are not shown for the cyclopentadienyl or phenyl groups. Primed atoms are related to unprimed ones via the crystallographic twofold rotational axis ($^1/4$, *y*, 0) passing through the zirconium atom.

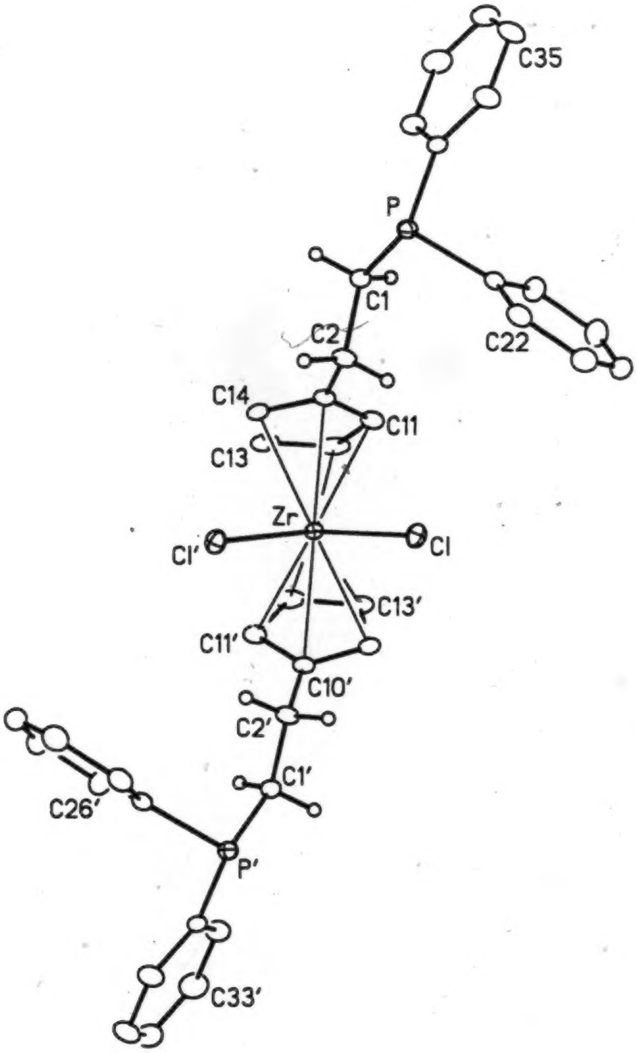

C35
P
C1
C2
C22
C14
C11
C13
Zr
Cl'
Cl
C13'
C11'
C10'
C2'
C1'
C26'
P'
C33'

Figure 3.2. Alternate view of compound **26** showing the orientation of the $CH_2CH_2PPh_2$ moieties.

Table 3.3 Selected Bond Lengths and Angles for $[(\eta^5\text{-}CH_2CH_2PPh_2)_2ZrCl_2]$ **(26)**

(a) Selected Interatomic Angles (Å)

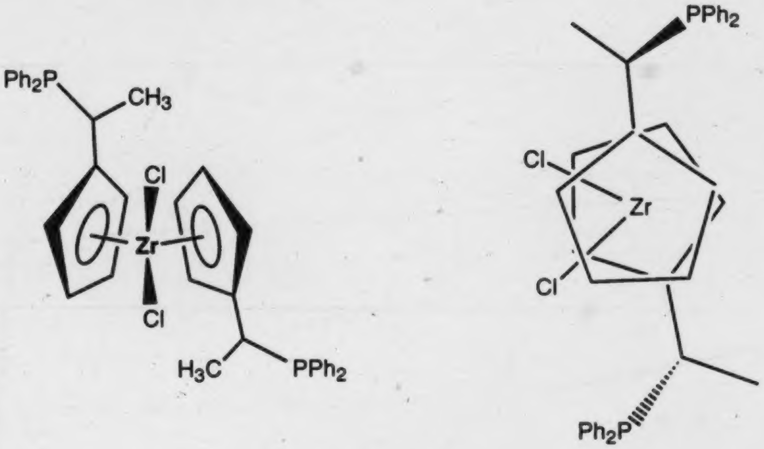
Atom1	Atom2	Distance
Zr	Cl	2.4448(6)
Zr	C(10)	2.565(2)
Zr	C(11)	2.509(2)
Zr	C(12)	2.473(2)
Zr	C(13)	2.462(2)
Zr	C(14)	2.534(2)
P	C(1)	1.850(2)
P	C(21)	1.841(2)
P	C(31)	1.837(2)
C(1)	C(2)	1.539(3)
C(2)	C(10)	1.498(3)
C(10)	C(11)	1.424(3)
C(10)	C(14)	1.400(3)
C(11)	C(12)	1.398(3)
C(12)	C(13)	1.408(4)
C(13)	C(14)	1.410(3)
C(21)	C(22)	1.384(3)
C(21)	C(26)	1.382(3)
C(22)	C(23)	1.387(4)
C(23)	C(24)	1.357(4)
C(24)	C(25)	1.375(4)
C(25)	C(26)	1.403(3)
C(31)	C(32)	1.380(4)
C(31)	C(36)	1.388(3)
C(32)	C(33)	1.386(4)
C(33)	C(34)	1.374(5)
C(34)	C(35)	1.362(5)
C(35)	C(36)	1.393(4)

(b) Selected Interatomic Angles (deg)

Atom1	Atom2	Atom3	Angle
Cl	Zr	Cl’	99.69(3)
C(1)	P	C(21)	98.73(9)
C(1)	P	C(31)	102.25(10)
C(21)	P	C(31)	99.89(9)
P	C(1)	C(2)	111.54(15)
C(1)	C(2)	C(10)	110.2(2)
C(2)	C(10)	C(11)	125.4(2)
C(2)	C(10)	C(14)	127.6(2)
C(11)	C(10)	C(14)	106.7(2)
C(10)	C(11)	C(12)	108.8(2)
C(11)	C(12)	C(13)	107.7(2)
C(12)	C(13)	C(14)	107.8(2)
C(10)	C(14)	C(13)	108.9(2)
P	C(21)	C(22)	118.4(2)
P	C(21)	C(26)	122.9(2)
C(22)	C(21)	C(26)	118.7(2)
C(21)	C(22)	C(23)	121.2(3)
C(22)	C(23)	C(24)	119.8(3)
C(23)	C(24)	C(25)	120.5(2)
C(24)	C(25)	C(26)	119.9(3)
C(21)	C(26)	C(25)	119.9(2)
P	C(31)	C(32)	125.0(2)
P	C(31)	C(36)	116.8(2)
C(32)	C(31)	C(36)	118.1(2)
C(31)	C(32)	C(33)	120.9(3)
C(32)	C(33)	C(34)	120.6(3)
C(33)	C(34)	C(35)	119.3(3)
C(34)	C(35)	C(36)	120.8(3)
C(31)	C(36)	C(35)	120.4(3)

Primed atoms are related to unprimed ones via the twofold rotational axis ($^1/4$, *y*, 0).

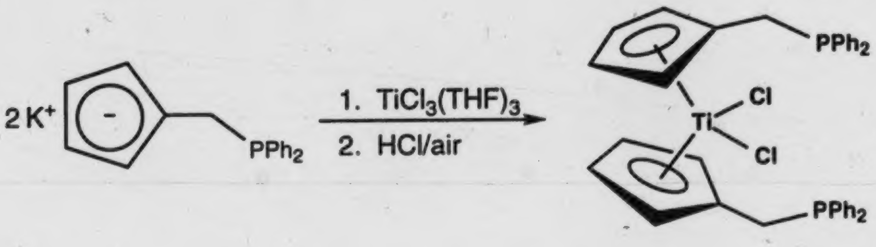
The presence of a ethyldiphenylphosphino group bound to each Cp ring has resulted in a slight asymmetry in the Zr-C bond lengths of compound **26**, with these distances decreasing steadily from 2.565(2) Å at the substituted carbon to 2.468(average) Å for C(12) and C(13). In addition, the asymmetry is also evident in the carbon-carbon bond angles within the Cp groups, where that of the substituted carbon is 106.7(2)° and the average for the unsubstituted carbons is 108.3°. The Cp(c)-Zr-Cp(c) angle and the Cp(c)-Zr bond lengths are remarkably similar to those found in Cp'_2ZrCl_2, with values of 130.9° and 2.205 (average) Å, respectively.



A

These differences in alkylphosphino arm orientation may have important implications in the formation of binuclear complexes, as will be discussed in the next chapter. From the orientation of the alkylphosphino substituents, which the X-ray structure indicates are bisecting the Cl-Zr-Cl angle and pointing in the same direction, compound **26** appears to be well set up for the formation of binuclear complexes through rotation about the Cp-alkyl bonds. It should be noted, however, that their orientation also suggests that formation of oligomers, in which the two arms bind to different metals, is possible.

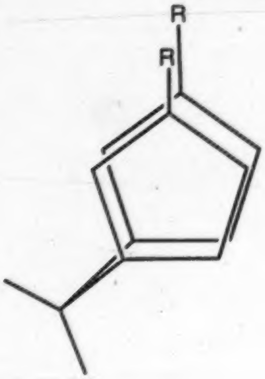
The titanocene-dichloride derivative with a methyldiphenyphosphino unit bound to the cyclopentadienyl ring, [η^5-$C_5H_4CH_2PPh_2)_2TiCl_2$] (**27**) was prepared by the reaction of K[$C_5H_4CH_2PPh_2$] (**22**) with $TiCl_3(THF)_3$, followed by oxidation with HCl, as shown below.



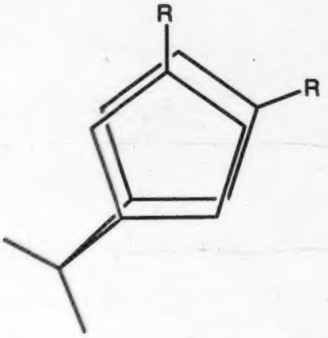
22 **27**

^{1}H NMR spectroscopy of this complex shows a methylene singlet at 3.51 ppm, with no resolvable phosphorus coupling, as was observed for the free ligand. The Cp resonances appear at 6.18 and 6.25 ppm, and this downfield shift relative to the free ligand was also observed for the titanocene dichloride derivative with a two-carbon spacer, [η^5-C_5H_4-$CH_2CH_2PPh_2)_2TiCl_2$] (**25**). The $^{31}P\{^1H\}$ NMR spectrum of compound **27** shows a large change from -16.3 for the free ligand, to a singlet at -9.6 ppm for the complexed ligand. This downfield shift contrasts with the results obtained in the complexes [(η^5-$C_5H_4CH_2$-$CH_2PPh_2)_2MCl_2$] (M = Ti (**25**), Zr (**26**)), in which coordination of the cyclopentadienyl unit to the metal results in essentially no change in the ^{31}P NMR spectrum. In compound **27**, phosphine coordination to the early metal is not expected as chelation should result in a significantly strained ring, although chelation of these ligand types has been observed in a similar zirconocene-type complex, [(η^5:η^1-$C_5H_4CMe_2PPh_2)_2ZrMe$][$MeB(C_6F_5)_3$].[12d] The downfield shift upon coordination of the C_5H_4 moiety to titanium is therefore likely due to the smaller cyclopentadienyl-PPh_2 separation in compound **27**, which results in the phosphine unit being closer to the metal. This presumably results in a large difference in the chemical environment compared to the free ligand. The zirconium-containing derivative [(η^5-$C_5H_4CH_2PPh_2)_2ZrCl_2$] (**28**) was prepared via reaction of K[$C_5H_4CH_2PPh_2$] (**22**) with $ZrCl_4$ or $ZrCl_4(THF)_2$ and has similar spectroscopic features to compound **27**. The similarity of the ^{31}P NMR chemical shift (δ = -9.7 ppm) provides further evidence that the phosphorus is not metal-bound, since one would expect a significant chemical-shift difference upon coordination to the two different metals.

Preparation of an *ansa*-metallocene dichloride was of interest in that the presence of a one-carbon linker between the two cyclopentadienyl rings would decrease the rotational freedom of the cyclopentadienyl units, the significance of which will be discussed in the next chapter of this thesis. In addition, the linker should decrease the Cp(c)-M-Cp(c) angle, resulting in easier substrate access to the metal center.[11] Reaction of $Li_2[Me_2C(C_5H_3CMe_2PPh_2)_2]$ (**24**) with $ZrCl_4$ afforded a bright yellow product, the $^{31}P\{^1H\}$ NMR spectrum of which showed the presence of two compounds, *rac*- and *meso*-[$Me_2C(C_5H_3CMe_2PPh_2)_2ZrCl_2$] (**29**) in a 2.8:1 ratio. As is often observed,[10] the meso and rac isomers have differing solubility properties, thus allowing for the separation of the two. The rac isomer was obtained spectroscopically pure, but the meso isomer was always found to be contaminated with the rac isomer. The $^{31}P\{^1H\}$ NMR spectrum of this complex is similar to that of [(η^5-$C_5H_4CMe_2PPh_2)_2ZrCl_2$],[2i] with a ^{31}P NMR chemical shift of 32.7 ppm. ^1H NMR spectroscopy on this compound shows three cyclopentadienyl hydrogen resonances at 5.07, 5.48 and 5.99 ppm, as well as doublets at 1.48 (J_{HP} = 13.0 Hz) and 1.75 (J_{HP} = 16.2 Hz). The key to determining whether the rac or meso isomer is obtained is the signal for the methyl hydrogens of the Me_2C linker. In the meso isomer, the methyl groups are in different chemical environments and are expected to have different chemical shifts, whereas in the rac isomer, which contains a C_2 rotation axis, the methyl groups are chemically equivalent as is shown below. In a mixture of the two isomers, three methyl-linker resonances are observed in the ^{1}H NMR spectrum, one of which corresponds to the methyl groups of the rac isomer, and the other two presumably are due to the two inequivalent methyl resonances in the meso isomer. A pure sample of the rac isomer shows only the single methyl resonance, as observed above.



meso-**29**



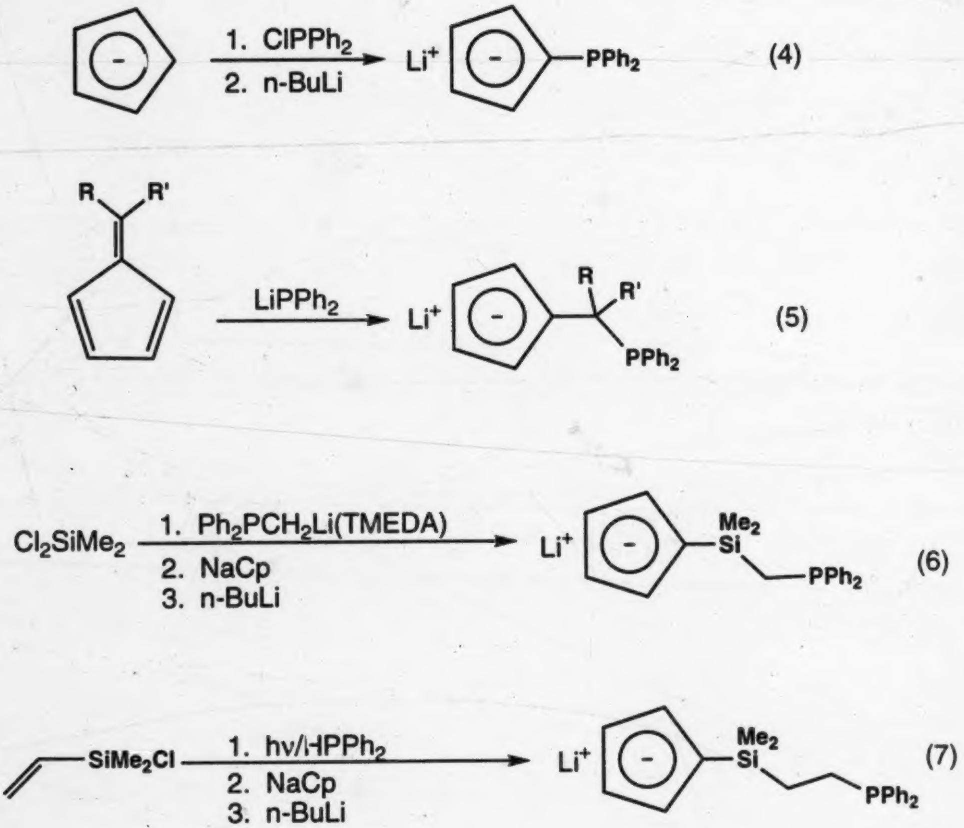
rac-**29**

Discussion

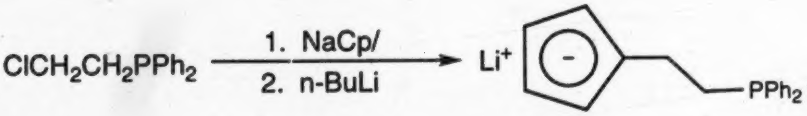
We were interested in preparing early-late heterobimetallic (ELHB) complexes in which early- and late-transition metals were held in close proximity by a pendant-phosphine-containing cyclopentadienyl ring, in which the cyclopentadienyl unit would be bound to the early-metal and the phosphine bound to the late-metal. Several ligands of this type have been prepared, as shown in Scheme 3.4 below, and the reactivity of their metallocene dichlorides with late-metal sources investigated.[2h-n, 3]

Several authors have reported the use of the ligand shown in equation (4), in the preparation of ELHB complexes.[2j-n, 3] We felt that a ligand having a PR$_2$ group directly

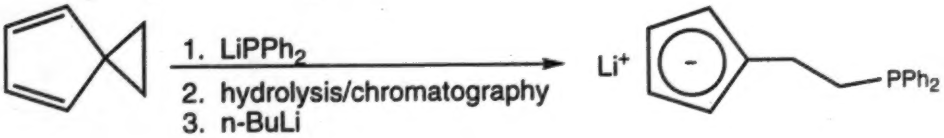
Scheme 3.4


-
1. ClPPh$_2$
2. n-BuLi
Li$^+$
-
PPh$_2$
(4)
R
R'
LiPPh$_2$
Li$^+$
-
R
R'
PPh$_2$
(5)
Cl$_2$SiMe$_2$
1. Ph$_2$PCH$_2$Li(TMEDA)
2. NaCp
3. n-BuLi
Li$^+$
-
Me$_2$
Si
PPh$_2$
(6)
SiMe$_2$Cl
1. hν/HPPh$_2$
2. NaCp
3. n-BuLi
Li$^+$
-
Me$_2$
Si
PPh$_2$
(7)

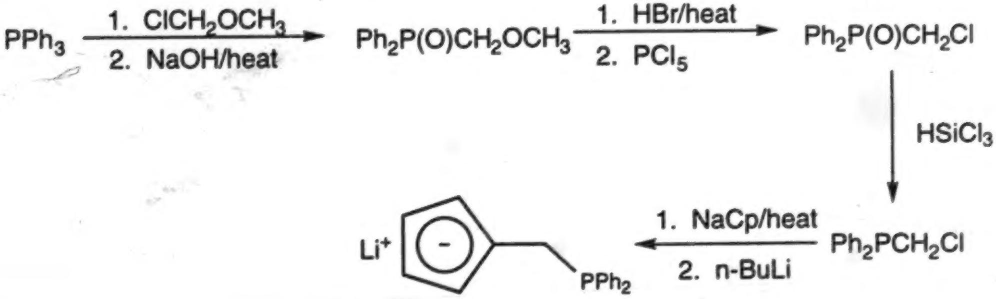
bound to the cyclopentadienyl moiety would be too rigid for the construction of heterobinuclear complexes capable of displaying metal-metal cooperativity effects. It seemed that with such a ligand the phosphines would prefer to bind in a cis manner to a late metal, as has been observed in several cases,[2k, m] resulting in a large metal-metal separation. Certainly, in the only example of such a complex binding trans at a late metal, the structure indicates a great deal of strain within the compound, with probably too little conformational flexibility to allow the ligand migrations from metal-to-metal, and the often accompanying breaking/formation of metal-metal bonds that seem to be necessary in cooperativity effects.[14] We wanted a ligand which, like dppm, was flexible enough to allow for the reversible formation of these metal-metal bonds.[14] It seemed that an obvious way to alleviate this problem would be to insert an alkyl spacer between the Cp and phosphine groups, like those shown in Scheme 3.4. "C_2" ligands, or those with a two-atom spacer had been reported previously by Schore,[15] shown in equation (6), and by Mathey *et al.*[2h] The ligand reported by Schore, $Li[C_5H_4SiMe_2CH_2PPh_2]$, while easy to prepare, was not the ideal ligand to start with, as we felt that the presence of two silicon-bound methyl groups might lead to problematic steric interactions in the preparation of ELHB complexes. The ligand $Li[C_5H_4CH_2CH_2PPh_2]$ had also been reported previously, by Mathey *et al*, and was prepared at that time via the reaction sequence shown below.



Reproducing their results proved impossible however, as the reaction consistently gave intractable mixtures, likely due to the strong basicity and poor nucleophilicity of the Cp anion, as some authors have reported the formation of $CH_2{=}CHPPh_2$ in this reaction via the dehydrohalogenation of $ClCH_2CH_2PPh_2$.[16a] Surprisingly perhaps, in view of the intractable mixtures obtained in our hands, these authors reported subsequent preparation of metallocene dichlorides and formation of ELHB complexes, using the ligand prepared by this route.[2h] Significantly, a later paper by Poilblanc did not use the ligand preparation reported earlier,[12a] but used another method which is shown below.[12b] Unfortunately, the reaction sequence outlined in the later report was not adequately documented, and has not yet to our knowledge been appropriately reported in the subsequent literature. Our current preparation is our own modification of this reaction.

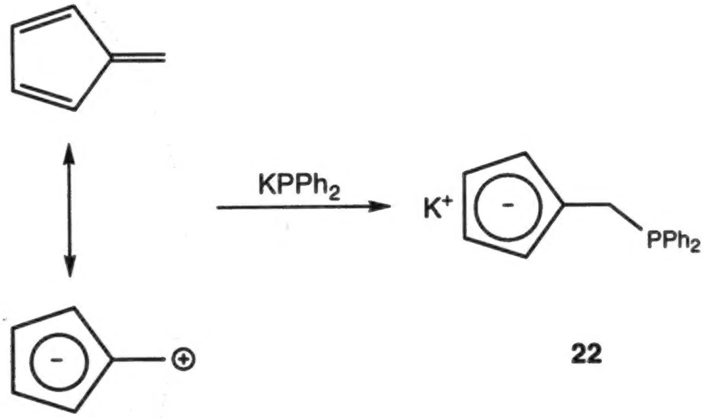

1. LiPPh2
2. hydrolysis/chromatography
3. n-BuLi
Li+
-
PPh2

Mathey *et al.* have also reported a synthesis for the ligand with a one-carbon spacer between the cyclopentadienyl and phosphine groups, $Li[C_5H_4CH_2PPh_2]$. This compound was prepared in several steps from PPh_3 and NaCp,[17] as shown below.


PPh3
1. ClCH2OCH3
2. NaOH/heat
Ph2P(O)CH2OCH3
1. HBr/heat
2. PCl5
Ph2P(O)CH2Cl
HSiCl3
Ph2PCH2Cl
1. NaCp/heat
2. n-BuLi
Li+
-
PPh2

This reaction did not seem very efficient to us, in that the preparation of Ph_2PCH_2Cl by this method is quite time consuming. However, $Ph_2P(BH_3)CH_2Cl$ may be prepared in two steps from Ph_2PH, BH_3SMe_2, n-BuLi and CH_2Cl_2,[18] and accordingly, we attempted a reaction similar to the last step shown above with this phosphinoborane and a large excess of NaCp. NMR spectra taken of the reaction mixture showed that the BH_3 group had been removed, presumably by the Cp^- anion, forming Ph_2PCH_2Cl cleanly, but subsequent chloride displacement by Cp^- proceeded sluggishly, with concomitant formation of a number of side products (as we had observed for the reaction of NaCp with $ClCH_2CH_2PPh_2$), so this route was abandoned. Since nucleophiles are known to add readily to the positively polarized C(6) carbon of fulvenes, this seemed to be an attractive alternative for the preparation of a ligand with a C_1 spacer, and in fact, was analogous to the route used by Erker.[12c] Although the preparation of fulvene is time consuming, we found that addition of $KPPh_2$ occurred readily to give the spectroscopically pure product, $K[C_5H_4CH_2PPh_2]$ (**22**), as is shown in Scheme 3.5.

Scheme 3.5



As will be discussed later in this thesis, we felt that the rotational flexibility of the cyclopentadienyl rings might hinder the formation of binuclear ELHB complexes. It seemed that an obvious way to decrease this flexibility was to prepare an *ansa*-metallocene, and we chose the fulvene route, analogous to the method used by Little and Stone,[19] due to the ease of preparing the fulvene shown in Scheme 3.2. Subsequent addition of two equivalents of diphenylphosphide anion provided an *ansa*-metallocene precursor, compound **24**, in good yield. Reaction of this ligand with $ZrCl_4$ afforded the *ansa* metallocene dichloride **29**, and the isomer obtained pure was shown by ^1H NMR to be the rac isomer.

At a late stage in this work, the synthesis of several cyclopentadienylmethyldiphenylphosphino ligands containing one or two alkyl substituents at the spacer methylene group was reported by Erker.[2i, 12d] Their objective was to use these ligands to prepare pendant-phosphine-containing metallocene dichlorides as metalloligands for late-transition metals in an analogous manner to ours. The structural differences between the crystallographically characterized $[(\eta^5\text{-}C_5H_4CHMePPh_2)_2ZrCl_2]$[2i], and $[(\eta^5\text{-}C_5H_4CH_2CH_2PPh_2)_2ZrCl_2]$ (**26**) may provide a useful contrast for the reactivity studies of these types of complexes with late-metal sources, as will be discussed in the next chapter.

Substantial problems were encountered in the initial part of this study due to misleading reports in the literature,[2h] and poor documentation of synthetic methodologies,[12b] particularly with respect to the preparation of the ligand $C_5H_4CH_2CH_2PPh_2$ and subsequent chemistry. Inspection of the literature regarding $[(\eta^5\text{-}C_5H_4CH_2CH_2PPh_2)_2ZrCl_2]$ (**26**) reveals that the product had been isolated as a yellowish oil.[2h, 16a] In our hands, this result was generally obtained when the product was impure, and we have found a convenient route for the preparation of usable quantities of this compound as an analytically pure white solid, as well as several other alkylphosphino-substituted-metallocene dichlorides.

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Chapter 4

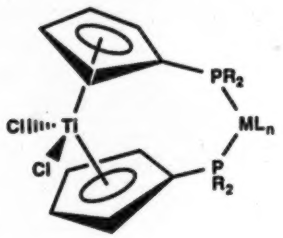
Heteronuclear Complexes Containing Early- and Late-Transition Metals Bridged by Cyclopentadienyl(alkyl)diphenylphosphines.

Introduction

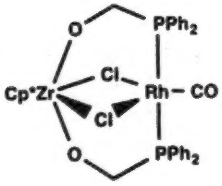
A variety of applications are known for transition metals that make specific use of their characteristic reactivities with regard to their position in the periodic table. Examples of these involving late metals include the hydroformylation reaction, and the Wacker process,[1] whereas early metals catalyze the Zeigler-Natta reaction,[2] and zirconium is used in the well known hydrozirconation reaction.[3] Early-and late-transition metals often exhibit complementary properties which potentially could lead to useful applications if these metal types could be combined. For example, late-metal complexes are typically electron rich and in low oxidation states and as such tend to bind π-acid ligands, and often participate in oxidative-addition reactions.[4] Early-metal-containing compounds, on the other hand, are often electron deficient by virtue of their low valence electron counts, and are typically in a high oxidation state which results in a strong affinity for hard Lewis bases such as oxygen donors.[5] Interest in complexes containing both early- and late-transition metals originates in the idea that two metals having substantially different properties could be used together in a cooperative way to effect substrate activation.[6] If two such metals are placed in close proximity, these electronic differences should result in a polar, bifunctional environment in which cooperativity effects between the two metals could allow for reactivities that are substantially different from individual mononuclear complexes. We were interested in preparing such compounds in the hope that this polar environment would assist in the activation of substrates such as carbon monoxide and carbon dioxide. It has been shown previously that group 8 to 10 metals supported on titanium oxides exhibit enhanced activity towards carbon monoxide hydrogenation, producing methane and higher hydrocarbons, compared to when these metals were supported on silica or alumina. This effect has been attributed to cooperative interactions between the early and late metals.[7]

One way to prepare early-late heterobimetallic (ELHB) complexes is to use systems that contain bifunctional ligands, in which one donor group of the ligand binds to the early metal and another donor group binds to the late metal.[8] The use of systematic ligand design and consequent preparation of ELHB complexes could lead to useful models for catalysts capable of converting inexpensive and readily available feedstocks such as carbon monoxide and carbon dioxide to useful chemicals such as methanol, formates, acetaldehyde or acetone.[7, 9]

Much previous work on these types of systems has been done with a variety of bridging ligands in order to hold the metals together. Two examples of which are shown below, involving the $C_5H_4PR_2$-type ligands (**A**)[8f-j] or OCH_2PPh_2-type ligands (**B**).[8b] Use of both ligand types in the preparation of ELHB complexes involves similar strategies in which the phosphine end binds to late metals whereas the other end, either a Cp or alkoxy moiety, both of which have a strong affinity for early metals, binds to this metal. Since many early-metal complexes contain cyclopentadienyl ligands, we decided to incorporate this functionality into our bridging ligand, similar to that shown in **A**.



A



B

Literature has shown that the ligand system shown in **A** would be too restricted to allow the substituents on a group 4 metallocene-dichloride derivative to be directed towards the late metal, reducing the possibility of metal-metal cooperativity effects.[8g] The ligands chosen should result in the orientation of the early-metal substituents towards the late metal, allowing for the transfer of groups between these metal centers, a key aspect in metal-metal cooperativity. As will be discussed later, we felt that a ligand of the type shown in **A**, with an alkyl spacer between the Cp and PR_2 units was a good candidate. In addition, there is a wealth of knowledge about both early-metal cyclopentadienyl and late-metal phosphine chemistry, and for these reasons we have chosen metallocene dichlorides of the type $[(C_5H_4(CR_2)_nPPh_2)_2MCl_2]$ where n = 1, 2 and M = Ti, Zr for the preparation of our ELHB complexes.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of prepurified argon with standard Schlenk techniques or in a nitrogen-filled Vac Atmospheres glovebox equipped with an HE-493 dri-train. Solvents were dried and distilled under nitrogen immediately before use. Sodium benzophenone was used as the drying agent except with CH_2Cl_2 which was distilled from P_2O_5. Deuterated THF and benzene were vacuum distilled from sodium benzophenone and deuterated dichloromethane from calcium hydride. Hydrated rhodium trichloride was purchased from Johnston-Matthey Ltd. Group 4 metal salts, $[(COD)PdCl_2]$ and $[(PhCN)_2PdCl_2]$ were purchased from Strem or Aldrich. $TiCl_4$ was used as received and $ZrCl_4$ was sublimed before use. $[Mo(CO)_4(COD)]$[10] and $[RhCl(CO)_2]_2$[11] were prepared via literature procedures, and 99% ^{13}CO was purchased from Isotec Inc. All other chemicals were purchased from Aldrich and used as received.

The ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AM-400 spectrometer operating at 400.1, 162.0 and 100.6 MHz for the respective nuclei. The internal deuterated solvent served as a lock for the spectrometer. All infrared spectra were run on a Nicolet 7199 FT interferometer as solids in Nujol or dichloromethane casts on KBr. The elemental analyses were performed by the microanalytical service within the department. Spectroscopic data for all compounds are given in Table 4.1.

Mass spectrometric analysis was performed by positive mode electrospray ionization on a Micromass ZabSpec Hybrid Sector-TOF. The liquid carrier was infused into the electrospray source by means of a Harvard syringe pump at a flow rate of 10 μL/minute. The sample solution was introduced *via* a 1 μL-loop-injector. Prepurified nitrogen was used as a spray pneumatic aid and filtered air as the bath gas, heated at *ca.* 80 °C. For low resolution, the mass spectra were acquired by magnet scan at a rate of 5 sec/decade. Data acquisition and processing was achieved by using the OPUS software package on a Digital Alpha station with VMS operating system.

Preparation of Compounds. (a) $[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)_2TiCl_2\text{-}Mo(CO)_4]$ (30). 28.6 mg (0.0905 mmol) of $[(COD)Mo(CO)_4]$ in 10 mL of THF was added via cannula to 61 mg (0.906 mmol) of $[(\eta^5\text{-}C_5H_4CH_2CH_2PPh_2)_2TiCl_2]$ (**25**) in 10 mL of THF. The red solution was stirred for 1 h and then the solvent was removed in vacuo. The red residue was recrystallized by dissolving in 5 mL of CH_2Cl_2 and adding 20 mL of MeOH dropwise, followed by stirring for 1 h. The red microcrystalline solid that had formed was washed with 2×10 mL of MeOH and 1×10 mL of Et_2O, and then dried in vacuo. Yield 30 mg, 40% of an analytically pure product. Anal. Calcd. for $C_{42}H_{36}P_2O_4\text{-}Cl_2TiMo$: C, 57.23%; H, 4.12%. Found: C, 57.11%; H, 3.96%.

Table 4.1 Spectroscopic Data for Compounds[a]

		NMR[c]	
compound:	IR (cm^{-1})[b]	$\delta(^{31}P\{^1H\})$ (ppm)	$\delta(^1H)$ (ppm)[e]
$[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)_2TiCl_2Mo(CO)_4]^d$ (30)	2023 (m, sh) 1927 (s) 1896 (vs)	26.6 (s, Mo-*P*)	6.24 (br, 8H $C_5\mathit{H}_4$) 2.45 (m, 4H, $CH_2\mathit{CH}_2PPh_2$) 2.55 (m, 4H, $\mathit{CH}_2CH_2PPh_2$)
$[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)_2ZrCl_2Mo(CO)_4]^d$ (31)	2022 (m, sh) 1928 (s) 1896 (vs)	26.6 (s, Mo-*P*)	6.37 (m, 4H, $C_5\mathit{H}_4$) 6.31 (m, 4H, $C_5\mathit{H}_4$) 2.55 (m, 8H, $\mathit{CH}_2\mathit{CH}_2PPh_2$
$[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)_2TiCl_2RhCl(CO)]_2$ (32a)	1974 (s)	26.3 (d, $^1J_{Rh\text{-}P}$=123.9 Hz, Rh-*P*)	6.40 (m, 8H, $C_5\mathit{H}_4$) 6.36 (m, 8H, $C_5\mathit{H}_4$) 3.09 (m, 8H $CH_2\mathit{CH}_2PPh_2$) 2.94 (m, 8H $\mathit{CH}_2\mathit{CH}_2PPh_2$)

Table 4.1 (continued)

$[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)_2TiCl_2RhCl(CO)]_2$ (32b)	1974 (s)	31.2 (d, $^1J_{\mathrm{Rh\text{-}P}}$=128.1 Hz, Rh-*P*)	7.22 (m, 4H $C_5\mathit{H}_4$) 6.91 (m, 4H $C_5\mathit{H}_4$) 6.67 (m, 4H $C_5\mathit{H}_4$) 6.08 (m, 4H $C_5\mathit{H}_4$) 3.09 (m, 8H $C\mathit{H}_2C\mathit{H}_2PPh_2$) 2.94 (m, 8H $C\mathit{H}_2C\mathit{H}_2PPh_2$)
$[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)_2ZrCl_2RhCl(CO)]_2$ (33a)	1974	26.0 (d, $^1J_{\mathrm{Rh\text{-}P}}$=124.0 Hz Rh-*P*)	6.28 (m, 8H, $C_5\mathit{H}_4$) 6.25 (m, 8H, $C_5\mathit{H}_4$) 3.06 (m, 8H $C\mathit{H}_2C\mathit{H}_2PPh_2$) 2.90 (m, 8H $C\mathit{H}_2C\mathit{H}_2PPh_2$)
$[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)_2ZrCl_2RhCl(CO)]_2$ (33b)	1968	30.8 (d, $^1J_{\mathrm{Rh\text{-}P}}$=126.7 Hz Rh-*P*)	7.01 (m, 4H $C_5\mathit{H}_4$) 6.71 (m, 4H $C_5\mathit{H}_4$) 6.46 (m, 4H $C_5\mathit{H}_4$) 6.03 (m, 4H $C_5\mathit{H}_4$) 3.11 (m, 8H $C\mathit{H}_2C\mathit{H}_2PPh_2$) 2.90 (m, 8H $C\mathit{H}_2C\mathit{H}_2PPh_2$)

Table 4.1 (continued)

$[((\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4CH_2PPh_2)_2TiCl_2RhCl(CO))_2]_2$ (34)	1973	31.9 (d, $^1J_{Rh\text{-}P}$=125.7 Hz, Rh-*P*)	6.59 (m, 8H C_5H_4) 6.55 (m, 8H C_5H_4) 3.94 (m, $^{2+4}J_{PH}$ = 3.5 Hz, 8H, CH_2PPh_2)
$[((\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4CH_2PPh_2)_2ZrCl_2RhCl(CO))_2]_2$[d] (35)	1977	31.6 (d, $^1J_{Rh\text{-}P}$=131.7 Hz, Rh-*P*)	6.44 (m, 8H, C_5H_4) 6.34 (m, 8H, C_5H_4) 3.99 (m $^{2+4}J_{PH}$ = 3.5 Hz, 8H, CH_2PPh_2)
$[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4CH_2PPh_2)_2TiCl_2PdCl_2]_2$ (36)		22.5 (s, Pd-*P*)	6.50 (m, 8H, C_5H_4) 6.47 (m, 8H, C_5H_4) 3.80 (m, $^{2+4}J_{PH}$ = 3.3 Hz, 8H, CH_2PPh_2)

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[a] Abbreviations used: for IR spectra, (vs) very strong; (s) strong; (m) medium, (sh) sharp; for NMR (m) multiplet, (dm) doublet of multiplets; [b] IR spectra recorded as a CH_2Cl_2 cast unless otherwise stated; [c] NMR spectra recorded in CD_2Cl_2; [d] IR spectra recorded in CH_2Cl_2 solution; [e] PPh_2 bound phenyl groups omitted

(b) [(μ-η^5:η^1-$C_5H_4CH_2CH_2PPh_2)_2ZrCl_2Mo(CO)_4$] (31). 72 mg (0.227 mmol) of [(COD)Mo$(CO)_4$] in 30 mL of THF was added via cannula to 163 mg (0.227 mmol) of [(η^5-$C_5H_4CH_2CH_2PPh_2)_2ZrCl_2$] **(26)** in 30 mL of THF. The yellow solution was stirred for 1.5 h then the solvent was removed in vacuo. The yellow residue was recrystallized by dissolving in CH_2Cl_2 and filtering if necessary, and then adding MeOH dropwise until a white solid formed. The solid was washed with 2×10 mL MeOH, then 1×10 mL Et_2O, followed by drying in vacuo. Yield 173 mg, 84 %. Anal. Calcd. for $C_{42}H_{36}P_2O_4Cl_2ZrMo$: C, 54.55%; H, 3.92%. Found: C, 54.56%; H, 3.88%.

(c) *α* **- and** *β* **-[(μ-η^5:η^1-$C_5H_4CH_2CH_2PPh_2)_2TiCl_2RhCl(CO)]_2$ (32a** and **b**, respectively). 400 mg (0.594 mmol) of [(η^5-$C_5H_4CH_2CH_2PPh_2)_2TiCl_2$] **(25)** in 125 mL of THF and 115.5 mg (0.297 mmol) of $[RhCl(CO)_2]_2$ in 125 mL of THF were simultaneously added dropwise to 250 mL of THF at -80°C over 1.5 h. The solution was warmed to room temperature and stirred for 1 h. The solvent was removed in vacuo and the residue recrystallized by dissolving in 100 mL of CH_2Cl_2, and then adding 100 mL of Et_2O. After 30 min of stirring, 40 mL of Et_2O were added, followed by stirring for an additional 30 min and solvent removal via cannula. The solid was washed with 3×10 mL of Et_2O and dried in vacuo. Yield 145 mg of analytically pure **32**, 30%. Removal of the solvent from the supernatant from above and recrystallization of the solid yielded a mixture of **32** and **33**. Yield 264 mg, total yield 80%. Anal. Calcd. for $C_{78}H_{72}Cl_6O_2P_4Ti_2Rh_2$: C, 55.78%; H, 4.32%. Found: C, 55.58%; H, 4.25%.

(d) *α* ***- and*** *β* **-[(μ-η^5:η^1-$C_5H_4CH_2CH_2PPh_2)_2ZrCl_2RhCl(CO)]_2$ (33a** and **b**, respectively). 127 mg (0.177 mmol) of [(η^5-$C_5H_4CH_2CH_2PPh_2)_2ZrCl_2$] **(26)** in 35 mL of THF and 34.2 mg (0.0878 mmol) of $[RhCl(CO)_2]_2$ in 35 mL of THF were simultaneously added to 75 mL of THF at -80°C over 30 minutes. The solution was warmed to room temperature and stirred for 1 h. The solvent was removed in vacuo and the yellow residue was recrystallized by dissolving in 10 mL of CH_2Cl_2, followed by the dropwise addition of 18 mL of Et_2O and stirring 45 min. The solvent was removed via cannula and the solid washed with 3×5 mL of Et_2O and dried in vacuo, yielding 116 mg, 74% of pure **34**. After 3 days in solution, a 2:1 mixture of **33a**:**b** forms. Anal. Calcd. for $C_{78}H_{72}Cl_6O_2$-$P_4Zr_2Rh_2$: C, 53.04%; H, 4.11%. Found: C, 52.95%; H, 3.86%.

(e) $[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4CH_2PPh_2)_2TiCl_2RhCl(CO)]_2$ (34). 37.9 mg (0.0975 mmol) of $[RhCl(CO)_2]_2$ in 10mL of THF was added to 126 mg (0.195 mmol) of $[(\eta^5\text{-}C_5H_4CH_2PPh_2)_2TiCl_2]$ (**27**) in 5 mL of THF. The red solution was stirred for 1 h during which time an orange precipitate formed. 5 mL of Et_2O was added dropwise, and then the solvent was removed via cannula. The solid was washed with 2×5 mL of Et_2O and dried in vacuo. Yield 50 mg, 31%. Anal. Calcd. for $C_{74}H_{64}P_4O_2Cl_6Ti_2Rh_2$: C, 54.75%; H, 3.97 %. Found: C, 54.59%; H, 3.89%.

(f) $[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4CH_2PPh_2)_2ZrCl_2RhCl(CO)]_2$ (35). 50 mg (0.0726 mmol) of $[(\eta^5\text{-}C_5H_4CH_2PPh_2)_2ZrCl_2]$ (**28**) in 10 mL of THF was added to 13.9 (0.0358 mmol) of $[RhCl(CO)_2]_2$ in 10 mL of THF and the yellow solution was stirred for 30 min. The solvent was removed in vacuo and the residue recrystallized from CH_2Cl_2/n-pentane. Yield 47 mg, 77%. Elemental analyses showed that the compound crystallized with 0.5 mole equivalents of CH_2Cl_2. Anal. Calcd. for $C_{74.5}H_{65}P_4O_2Cl_7Zr_2Rh_2$: C, 51.06%; H, 3.74%; Cl, 14.16%. Found: C, 51.01%; H, 3.63%; Cl, 13.71%.

(g) $[((\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4CH_2PPh_2)_2TiCl_2PdCl_2)_2]$ (36). 9.5 mg (0.0333 mmol) of $[(COD)PdCl_2]$ in 5 mL of CH_2Cl_2 was added to 21.5 mg (0.0333 mmol) of $[(\eta^5\text{-}C_5H_4CH_2PPh_2)_2TiCl_2]$ (**25**) in 5 mL of CH_2Cl_2. The solution was stirred for 30 min and then the solvent removed in vacuo. The red residue was recrystallized by dissolving in 2 mL of CH_2Cl_2 and adding 4 mL of MeOH dropwise, followed by stirring for 30 min. The solvent was removed via cannula and the solid washed with 3×5 mL of MeOH and dried in vacuo. Yield 15 mg, 54%. Anal. Calcd. for $C_{72}H_{64}P_4Cl_8Ti_2Pd_2$: C, 52.56%; H, 3.92%. Found: C, 52.22%; H, 3.93%.

X-ray Data Collection. X-ray data collection and structure solutions were carried out by Dr. R. McDonald. Red and pale yellow crystals of $[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)_2TiCl_2Mo(CO)_4]$ (**30**) and $[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)_2ZrCl_2\text{-}Mo(CO)_4]$ (**31**), respectively, suitable for X-ray diffraction were obtained by diffusion of MeOH into a concentrated CH_2Cl_2 solution of the compounds. The crystals were mounted in a glass capillary under CH_2Cl_2 vapor to minimize decomposition or solvent loss. Red crystals of $[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)_2TiCl_2RhCl(CO)]_2$ (**32**) and $[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)_2TiCl_2RhCl(CO)]_2$ (**34**) were obtained by diffusion of Et_2O into CH_2Cl_2 solutions of these compounds. See Tables 4.2 and 4.3 for experimental details. The structures were solved by direct methods, using the SHELXS–86[12] software package.

Results and Compound Characterization.

Owing to the vast literature concerning early-metal Cp chemistry and the well known late-metal phosphine chemistry, we decided to use the metallocene dichlorides with Cp-bound phosphine arms as metalloligands for mid or late transition-metal centers. It was hoped that these metallocene dichlorides would form ligand-bridged structures analogous to those obtained with dppm in which the metals are held in close proximity by the bidentate ligand, without the requirement of a metal-metal bond. We felt that the use of cyclopentadienylphosphines, containing an alkyl spacer between the Cp and PR_2 groups might result in the orientation of the early-metal substituents towards the late metal, thus enhancing the chance for cooperativity between the two metal centers.

At the time this study was undertaken, very little had been reported on such compounds, particularily with respect to ligands containing a C_1 spacer. Poilblanc[8d] had

Table 4.2. Crystallographic Experimental Details for Compounds **30** and **31**

Compound:	$[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)_2\text{-}TiCl_2Mo(CO)_4]$ (**30**)•0.5 CH_2Cl_2	$[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)_2\text{-}ZrCl_2Mo(CO)_4]$ (**31**)•0.5 CH_2Cl_2
A. Crystal Data		
formula	$C_{42.5}H_{37}Cl_3MoO_4P_2Ti$	$C_{42.5}H_{37}Cl_3MoO_4P_2Zr$
formula weight	923.85	967.17
crystal dimensions (mm)	0.39 × 0.21 × 0.16	0.53 × 0.35 × 0.30
crystal system	triclinic	triclinic
space group	$P\overline{1}$ (No. 2)	$P\overline{1}$ (No. 2)
unit cell parameters[a]		
a (Å)	13.336 (2)	13.4643 (11)
b (Å)	13.547 (3)	13.553 (2)
c (Å)	12.330 (2)	12.4283 (15)
α (deg)	104.46 (2)	104.568 (11)
β (deg)	107.996 (13)	108.050 (8)
γ(deg)	77.340 (14)	77.489 (8)
V (Å^3)	2026.9 (7)	2063.1 (4)
Z	2	2
ρ_{calcd} (g cm^{-3})	1.514	1.557
μ (mm^{-1})	0.825	0.869

Table 4.2 (cont.)
B. Data Collection and Refinement Conditions

diffractometer	Enraf-Nonius CAD4[b]	Enraf-Nonius CAD4[b]
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	–50	–50
scan type	θ–2θ	θ–2θ
data collection 2θ limit (deg)	50.0	50.0
total data collected	7410 ($0 \leq h \leq 15$, $-15 \leq k \leq 16$, $-14 \leq l \leq 13$)	7517 ($-14 \leq h \leq 15$, $-15 \leq k \leq 16$, $0 \leq l \leq 14$)
independent reflections	7073	7072
number of observations (NO)	3404 ($F_o^2 \geq 2\sigma(F_o^2)$)	4563 ($F_o^2 \geq 2\sigma(F_o^2)$)
structure solution method	direct methods (SHELXS–86[c])	direct methods (SHELXS–86[c])
refinement method	full-matrix least-squares on F^2 (SHELXL–93[d])	full-matrix least-squares on F^2 (SHELXL–93[d])
absorption correction method	Gaussian integration (face-indexed)	DIFABS[e]
range of transmission factors	0.8878–0.8367	1.135–0.800
data/restraints/parameters	7071 [$F_o^2 \geq -3\sigma(F_o^2)$]/3[e]/482	7069 [$F_o^2 \geq -3\sigma(F_o^2)$]/3[f]/482
goodness-of-fit (S)[f]	1.007 [$F_o^2 \geq -3\sigma(F_o^2)$]	1.023 [$F_o^2 \geq -3\sigma(F_o^2)$]
final *R* indices[g]		
$F_o^2 > 2\sigma(F_o^2)$	$\boldsymbol{R_1} = \mathbf{0.0760}$, $wR_2 = 0.1663$	$\boldsymbol{R_1} = \mathbf{0.0703}$, $wR_2 = 0.1728$

Table 4.2 (cont.)

all data	$R_1 = 0.2195$, $\mathbf{wR_2 = 0.2291}$	$R_1 = 0.1525$, $\mathbf{wR_2 = 0.2274}$
largest difference peak and hole	1.053 and –1.095 e Å^{-3}	1.401 and –1.256 e Å^{-3}

[a] Obtained from least-squares refinement of 24 reflections with 20.0° < 2θ < 23.9° for compound **30**, and 24 reflections with 19.8° < 2θ < 23.8° for compound **31**.

[b] Programs for diffractometer operation and data collection were those supplied by Enraf-Nonius.

[c] Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467–473.

[d] Sheldrick, G. M. *SHELXL-93*. Program for crystal structure determination. University of Göttingen, Germany, 1993. Refinement on F_o^2 for all reflections except for 2 having $F_o^2 < -3\sigma(F_o^2)$ for compound **30** and except for 3 having $F_o^2 < -3\sigma(F_o^2)$ for compound **31**. Weighted *R*-factors wR_2 and all goodnesses of fit S are based on F_o^2; conventional *R*-factors R_1 are based on F_o, with F_o set to zero for negative F_o^2. The observed criterion of $F_o^2 > 2\sigma(F_o^2)$ is used only for calculating R_1, and is not relevant to the choice of reflections for refinement. *R*-factors based on F_o^2 are statistically about twice as large as those based on F_o, and *R*-factors based on ALL data will be even larger.

[e] An idealized geometry was imposed on the inversion-disordered CH_2Cl_2 solvent molecule by setting d(Cl(3)–C(99)) = d(Cl(3')–C(99)) = 1.80(1) Å and d(Cl(3)···Cl(3')) = 2.95(1) Å for compounds **30** and **31**.

[f] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [s^2(F_o^2) + (a_oP)^2 + a_1P]^{-1}$ where a_o = 0.0988, a_1 = 0 for compound **30** and a_0 = 0.1170 and a_1 = 16.5289 for compound **31**; $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3)$.

[g] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Table 4.3. Crystallographic Experimental Details for Compounds **32** and **34**.

compound:	$[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4\ CH_2CH_2PPh_2)_2\text{-}TiCl_2RhCl(CO)]_2]_2$ (**32**)	$[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4\ CH_2PPh_2)_2\text{-}TiCl_2RhCl(CO)]_2]_2$ (**34**)$\cdot CH_2Cl_2$
A. Crystal Data		
formula	$C_{78}H_{72}Cl_6O_2P_4Rh_2Ti_2$	$C_{75}H_{66}Cl_8O_2P_4Rh_2Ti_2$
formula weight	1679.56	1708.38
crystal dimensions (mm)	0.20 × 0.18 × 0.04	0.48 × 0.35 × 0.06
crystal system	monoclinic	triclinic
space group	C2/c (No. 15)	$P\overline{1}$ (No. 2)
unit cell parameters[a]		
a (Å)	36.654 (3)	13.955 (3)
b (Å)	12.0072 (12)	13.969 (4)
c (Å)	16.332 (3)	19.176 (4)
α (deg)		89.70 (2)
β (deg)	92.771 (3)	88.57 (2)
γ (deg)		82.45 (2)
V (Å^3)	7179.6 (18)	3704.6 (14)
Z	4	2
ρ_{calcd} (g cm^{-3})	1.554	1.532
μ (mm^{-1})	1.026	1.065

Table 4.3 (cont.).

B. Data Collection and Refinement Conditions

diffractometer	Enraf-Nonius KappaCCD[b]	Enraf-Nonius CAD4[b]
radiation (λ [Å])	Mo Kα (0.71073)	Mo Kα (0.71073)
monochromator	incident-beam, graphite crystal	incident-beam, graphite crystal
temperature (°C)	–173	–50
scan type	mixture of ϕ rotations and ω scans	θ–2θ
data collection 2θ limit (deg)	52.75	50.0
total data collected	7273 ($0 \leq h \leq 45$, $0 \leq k \leq 14$, $-20 \leq l \leq 20$)	12532 ($-16 \leq h \leq 16$, $-16 \leq k \leq 16$, $0 \leq l \leq 22$)
independent reflections	7273	12119
number of observations (NO)	4284 ($F_o^2 \geq 2\sigma(F_o^2)$)	6583 ($F_o^2 \geq 2\sigma(F_o^2)$)
structure solution method	direct methods (SHELXS–86[c])	direct methods (SHELXS–86[c])
refinement method	full-matrix least-squares on F^2 (SHELXL–93[d])	full-matrix least-squares on F^2 (SHELXL–93[d])
absorption correction method		semiempirical
range of transmission factors		0.9899–0.7648
data/restraints/parameters	7273 [$F_o^2 \geq -3\sigma(F_o^2)$] / 0 / 424	12119 [$F_o^2 \geq -3\sigma(F_o^2)$]/3[e]/838
goodness-of-fit (S)[f]	1.015 [$F_o^2 \geq -3\sigma(F_o^2)$]	1.041 [$F_o^2 \geq -3\sigma(F_o^2)$]
final R indices[g]		
$F_o^2 > 2\sigma(F_o^2)$	$R_1 = 0.0576$, $wR_2 = 0.1050$	$R_1 = 0.0827$, $wR_2 = 0.1912$
all data	$R_1 = 0.1233$, $wR_2 = 0.1232$	$R_1 = 0.1622$, $wR_2 = 0.2395$
largest difference peak and hole	1.030 and –0.664 e Å^{-3}	1.773 and –1.164 e Å^{-3}

Table 4.3 (cont.).

[a] For compound **36**, obtained from least-squares refinement of 24 reflections with $22.0° < 2\theta < 25.8°$

[b] Programs for diffractometer operation and data collection were those supplied by Enraf-Nonius.

[c] Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

[d] Sheldrick, G. M. *SHELXL-93*. Program for crystal structure determination. University of Göttingen, Germany, 1993. Refinement on F_o^2 for all reflections (all of these having $F_o^2 \geq -3\sigma(F_o^2)$). Weighted *R*-factors wR_2 and all goodnesses of fit *S* are based on F_o^2; conventional *R*-factors R_1 are based on F_o, with F_o set to zero for negative F_o^2. The observed criterion of $F_o^2 > 2\sigma(F_o^2)$ is used only for calculating R_1, and is not relevant to the choice of reflections for refinement. *R*-factors based on F_o^2 are statistically about twice as large as those based on F_o, and *R*-factors based on ALL data will be even larger.

[e] Distances within the solvent dichloromethane molecule for compound **36** were fixed as follows: d(Cl(7)–C(111)) = d(Cl(8)–C(111)) = 1.80(1) Å; d(Cl(7)–Cl(8)) = 2.95(1) Å (to maintain an idealized Cl(7)–C(111)–Cl(8) bond angle of 110°).

[f] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (a_0P)^2 + a_1P]^{-1}$ where $a_0 = 0.0499$, $a_1 = 0$ for compound (**32** or **33**) and $a_0 = 0.1141$, $a_1 = 1.7430$ for compound **36**; where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[g] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

reported a seemingly convenient route to a ligand with a C_2 spacer, so it was decided to begin the investigation here.

We began by preparing *cis*-$[(\mu\text{-}\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)_2MCl_2Mo(CO)_4]$ (M = Ti (**30**), Zr (**31**)), in which a C_2 spacer linked the Cp and the PPh_2 groups. Although these compounds had been previously reported, their characterization was inadequate,[8d] as will be discussed in detail later in this chapter. In addition, it was of interest to compare the structures of **30** and **31** with the known compound, $[(\mu\text{-}\eta^5{:}\eta^1\text{-}C_5H_4PPh_2)_2\text{-}ZrCl_2Mo(CO)_4]$ (**A**) in which the PR_2 groups are bound directly to the Cp moiety.[8g] One of our interests in this study was to obtain a structural comparison between ELHB complexes bridged by these cyclopentadienyl phosphines, in which the functional groups were either directly linked or connected by C_1 and C_2 spacers.

Compounds **30** and **31** were prepared via the reaction of $[(\eta^5\text{-}C_5H_4CH_2CH_2PPh_2)_2MCl_2]$ M = Ti (**25**), Zr (**26**) with (COD)Mo(CO)$_4$, which results in facile displacement of the labile diene group. The ^{31}P chemical shift upon coordination of the phosphino groups of $[(\eta^5\text{-}C_5H_4CH_2CH_2PPh_2)_2MCl_2]$ (M = Ti (**25**), Zr (**26**)) to the molybdenum center changes from -16.5 ppm (for both **25** and **26**) to 26.6 and 26.5 ppm (both singlets), respectively. The Cp hydrogens in the ^1H NMR spectrum of compound **28** are apparently coincidently degenerate and resonate at 6.24 ppm whereas the two methylene resonances of the phosphine arms are complex multiplets at 2.55 and 2.45 ppm. The ^1H NMR spectrum of compound **31** is similar to that of **30** except the Cp region now shows the expected AA'BB' multiplets, centered at 6.34 ppm and the resonances for the two methylene hydrogen groups appear as overlapping multiplets, centered at 2.55 ppm. The solution IR spectra of compounds **30** and **31** are virtually identical, with carbonyl bands at 2023, 1928 and 1896 cm^{-1} for **30** and 2022, 1927 and 1896 cm^{-1} for **31**. Moreover, and the carbonyl band pattern is similar to that of

(COD)Mo(CO)$_4$, indicating that the phosphines, like the COD moiety, are bound to the molybdenum center in a cis arrangement. To confirm the structures of compound **30** and **31**, and to compare the differences due to the different Group 4 metals, their structures were determined by single crystal X-ray techniques. Both compounds crystallized in the $P\overline{1}$ space group (No. 2) with 0.5 mole equivalents of CH_2Cl_2, and both have very similar cell parameters. In fact, both are isostructural, with only subtle differences resulting from the two different metallic radii (Ti = 1.324 Å, Zr = 1.454 Å).[13] Although the pendant phosphines presumably can have a range of orientations in the $[(\eta^5\text{-}C_5H_4\text{-}CH_2CH_2PPh_2)_2MCl_2]$ M = Ti (**25**), Zr (**26**) complexes, the molybdenum center has served to bring both alkyldiphenylphosphino arms together at this metal center, such that compounds **25** and **26** function as chelating metalloligands to Mo. The general features of the X-ray structures of complexes **30** and **31** are quite similar, with pseudotetrahedral ligand arrangements around the group 4 metal and pseudooctahedral geometries about molybdenum, with the phosphines of the $C_5H_4CH_2CH_2PPh_2$ units bound cis to this metal. Figure 4.1 shows a perspective view of the Zr complex **31** while Figure 4.1.1 shows an alternate view of the same molecule looking down the Cp-Cp vector. The drawings for the Ti analogue **30** are not shown since they are essentially identical and the numbering scheme is the same. Selected bond lengths and angles for both compounds are given in Tables 4.4 and 4.5, respectively. The structural results confirm that the binuclear framework has been achieved in which the early and mid-transition metals are bridged by the $C_5H_4CH_2CH_2PPh_2$ ligands. Metal-metal separations of 6.895 Å and 6.945 Å in compounds **30** and **31**, respectively, rule out any group 4 metal-molybdenum bonding interaction. As shown in Figure 4.1.1, the cyclopentadienyl groups are staggered slightly, where the angle subtended by the C(13)-C(14) and C(6)-C(7)

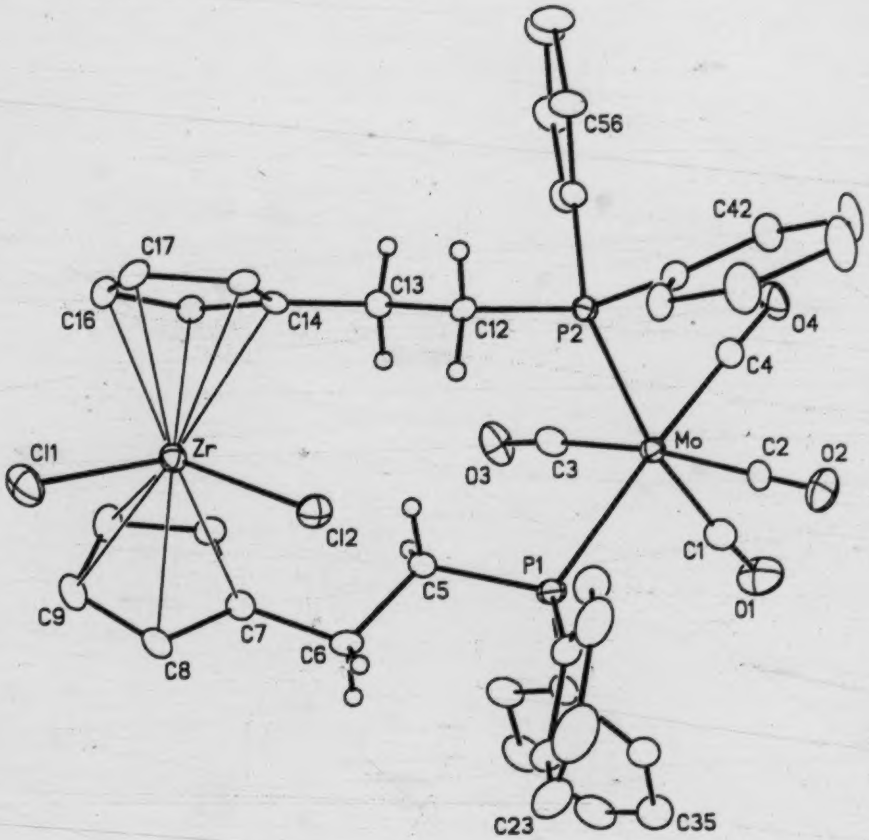

C56
C42
C17
C13
C16
C14
C12
P2
O4
C4
Cl1
Zr
Mo
C2
O2
O3
C3
Cl2
C1
P1
C5
O1
C9
C7
C6
C8
C23
C35

Figure 4.1. Perspective view of the $[(\eta^5\text{-}C_5H_4CH_2CH_2PPh_2)_2ZrCl_2Mo(CO)_4]$ (31) molecule showing the atom labelling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters for the methylene groups of the $\eta^5\text{-}C_5H_4CH_2CH_2PPh_2$ ligands, and are not shown for the cyclopentadienyl and phenyl groups.

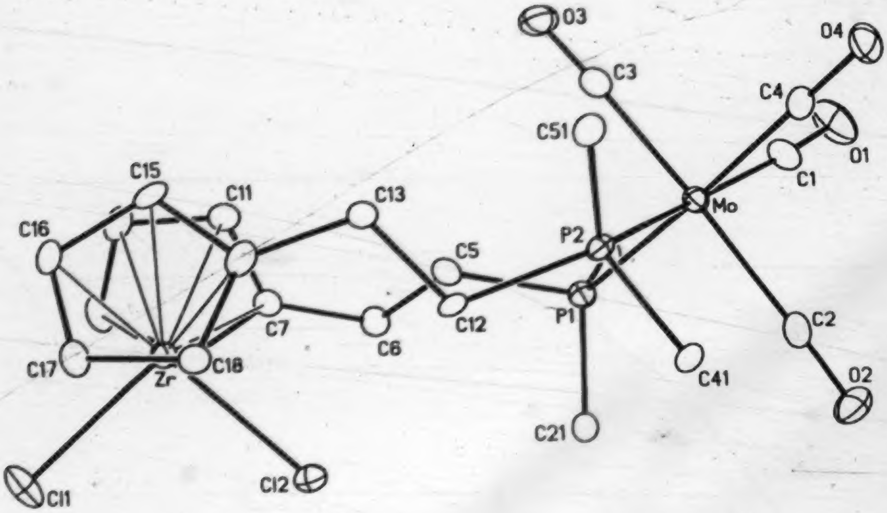

O3
O4
C3
C4
C51
O1
C1
C15
C11
C13
Mo
C16
P2
C5
P1
C7
C12
C2
C6
C17
Zr
C18
C41
O2
C21
Cl1
Cl2

Figure 4.1.1. Alternate view of compound **31** showing the orientation of the $ZrCl_2$ moiety.

Table 4.4 Selected Bond Lengths and Angles for Compound 30.

(a) Selected Interatomic Distances (Å)

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Mo	P(1)	2.535(3)	P(2)	C(12)	1.826(10)
Mo	P(2)	2.535(3)	P(2)	C(41)	1.812(11)
Mo	C(1)	1.968(12)	P(2)	C(51)	1.831(11)
Mo	C(2)	2.067(13)	O(1)	C(1)	1.144(14)
Mo	C(3)	1.978(13)	O(2)	C(2)	1.132(13)
Mo	C(4)	1.965(11)	O(3)	C(3)	1.165(14)
Ti	Cl(1)	2.351(3)	O(4)	C(4)	1.176(13)
Ti	Cl(2)	2.325(4)	C(5)	C(6)	1.544(14)
Ti	C(7)	2.487(11)	C(6)	C(7)	1.50(2)
Ti	C(8)	2.422(12)	C(7)	C(8)	1.407(14)
Ti	C(9)	2.393(11)	C(7)	C(11)	1.43(2)
Ti	C(10)	2.333(12)	C(8)	C(9)	1.41(2)
Ti	C(11)	2.375(11)	C(9)	C(10)	1.35(2)
Ti	C(14)	2.431(11)	C(10)	C(11)	1.425(15)
Ti	C(15)	2.384(12)	C(12)	C(13)	1.498(14)
Ti	C(16)	2.344(12)	C(13)	C(14)	1.534(13)
Ti	C(17)	2.371(11)	C(14)	C(15)	1.388(15)
Ti	C(18)	2.437(12)	C(14)	C(18)	1.42(2)
P(1)	C(5)	1.816(11)	C(15)	C(16)	1.39(2)
P(1)	C(21)	1.835(12)	C(16)	C(17)	1.42(2)
P(1)	C(31)	1.850(11)	C(17)	C(18)	1.398(15)

(b) Selected Interatomic Angles (deg)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
P(1)	Mo	P(2)	100.64(10)	P(2)	Mo	C(4)	85.4(4)
P(1)	Mo	C(1)	90.0(4)	C(1)	Mo	C(2)	89.0(5)
P(1)	Mo	C(2)	90.9(3)	C(1)	Mo	C(3)	89.4(6)
P(1)	Mo	C(3)	82.9(3)	C(1)	Mo	C(4)	84.0(5)
P(1)	Mo	C(4)	173.5(4)	C(2)	Mo	C(3)	173.6(5)
P(2)	Mo	C(1)	169.3(4)	C(2)	Mo	C(4)	91.5(5)
P(2)	Mo	C(2)	89.2(3)	C(3)	Mo	C(4)	94.4(5)
P(2)	Mo	C(3)	93.4(4)	Cl(1)	Ti	Cl(2)	93.54(14)

Table 4.4 (cont.)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
Mo	P(1)	C(5)	112.7(4)	C(8)	C(9)	C(10)	109.3(10)
Mo	P(2)	C(12)	124.7(4)	C(9)	C(10)	C(11)	108.6(11)
Mo	C(1)	O(1)	173.3(11)	C(7)	C(11)	C(10)	107.2(10)
Mo	C(2)	O(2)	179.0(10)	P(2)	C(12)	C(13)	113.3(7)
Mo	C(3)	O(3)	173.9(12)	C(12)	C(13)	C(14)	115.8(9)
Mo	C(4)	O(4)	176.9(11)	C(13)	C(14)	C(15)	126.5(10)
P(1)	C(5)	C(6)	120.5(8)	C(13)	C(14)	C(18)	125.5(10)
C(5)	C(6)	C(7)	112.7(10)	C(15)	C(14)	C(18)	107.4(10)
C(6)	C(7)	C(8)	128.0(11)	C(14)	C(15)	C(16)	110.2(11)
C(6)	C(7)	C(11)	125.6(10)	C(15)	C(16)	C(17)	106.4(10)
C(8)	C(7)	C(11)	106.4(10)	C(16)	C(17)	C(18)	108.9(10)
C(7)	C(8)	C(9)	108.3(11)	C(14)	C(18)	C(17)	107.2(10)

Table 4.5 Selected Bond Lengths and Angles for Compound 31

(a) Selected Interatomic Distances (Å)

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Mo	P(1)	2.539(2)	P(2)	C(12)	1.837(8)
Mo	P(2)	2.540(2)	P(2)	C(41)	1.826(9)
Mo	C(1)	1.991(12)	P(2)	C(51)	1.838(9)
Mo	C(2)	2.071(11)	O(1)	C(1)	1.155(13)
Mo	C(3)	1.997(11)	O(2)	C(2)	1.146(12)
Mo	C(4)	2.006(10)	O(3)	C(3)	1.148(12)
Zr	Cl(1)	2.431(3)	O(4)	C(4)	1.132(11)
Zr	Cl(2)	2.412(2)	C(5)	C(6)	1.542(13)
Zr	C(7)	2.554(9)	C(6)	C(7)	1.497(13)
Zr	C(8)	2.542(9)	C(7)	C(8)	1.404(13)
Zr	C(9)	2.513(9)	C(7)	C(11)	1.413(13)
Zr	C(10)	2.474(9)	C(8)	C(9)	1.382(14)
Zr	C(11)	2.487(9)	C(9)	C(10)	1.412(15)
Zr	C(14)	2.541(9)	C(10)	C(11)	1.402(13)
Zr	C(15)	2.511(9)	C(12)	C(13)	1.536(12)
Zr	C(16)	2.475(9)	C(13)	C(14)	1.515(12)
Zr	C(17)	2.502(9)	C(14)	C(15)	1.412(12)
Zr	C(18)	2.541(8)	C(14)	C(18)	1.408(13)
P(1)	C(5)	1.824(9)	C(15)	C(16)	1.415(13)
P(1)	C(21)	1.823(10)	C(16)	C(17)	1.401(14)
P(1)	C(31)	1.833(9)	C(17)	C(18)	1.389(13)

(b) Selected Interatomic Angles (deg)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
P(1)	Mo	P(2)	100.87(8)	P(2)	Mo	C(4)	85.6(3)
P(1)	Mo	C(1)	90.3(3)	C(1)	Mo	C(2)	89.3(4)
P(1)	Mo	C(2)	90.9(3)	C(1)	Mo	C(3)	88.9(4)
P(1)	Mo	C(3)	83.2(3)	C(1)	Mo	C(4)	83.3(4)
P(1)	Mo	C(4)	172.8(3)	C(2)	Mo	C(3)	173.8(4)
P(2)	Mo	C(1)	168.7(3)	C(2)	Mo	C(4)	92.3(4)
P(2)	Mo	C(2)	88.9(3)	C(3)	Mo	C(4)	93.3(4)
P(2)	Mo	C(3)	94.1(3)	Cl(1)	Zr	Cl(2)	96.30(10)

Table 4.5 (cont.)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
Mo	P(1)	C(5)	112.2(3)	C(8)	C(9)	C(10)	108.2(8)
Mo	P(2)	C(12)	125.1(3)	C(9)	C(10)	C(11)	107.0(9)
Mo	C(1)	O(1)	173.9(9)	C(7)	C(11)	C(10)	109.0(9)
Mo	C(2)	O(2)	178.3(9)	P(2)	C(12)	C(13)	112.2(6)
Mo	C(3)	O(3)	174.9(9)	C(12)	C(13)	C(14)	113.6(7)
Mo	C(4)	O(4)	177.6(9)	C(13)	C(14)	C(15)	123.2(8)
P(1)	C(5)	C(6)	119.8(6)	C(13)	C(14)	C(18)	128.4(8)
C(5)	C(6)	C(7)	113.1(8)	C(15)	C(14)	C(18)	107.7(8)
C(6)	C(7)	C(8)	127.1(9)	C(14)	C(15)	C(16)	107.1(8)
C(6)	C(7)	C(11)	126.5(9)	C(15)	C(16)	C(17)	108.5(8)
C(8)	C(7)	C(11)	106.3(9)	C(16)	C(17)	C(18)	107.9(8)
C(7)	C(8)	C(9)	109.5(9)	C(14)	C(18)	C(17)	108.8(8)

vectors are 32.9° for both compounds and seems to indicate that these groups may rotate about the Cp-early metal bond to find the most sterically favourable orientation. This drawing also shows that the molybdenum atom is located to the side of the pocket created by the canted cyclopentadienyl rings, with Mo-M-X angles, where X is the bisector of the Cl-M-Cl angle, of 103.1° for compound **30** (M = Ti) and 104.4° for **31** (M = Zr), indicating that the early-metal substituents are directed away from the molybdenum center. Despite the presence of an ethyldiphenylphosphine unit bound to the cyclopentadienyl rings, the Cp(centroid)-M-Cp(centroid) angles of 128.9° for compound **30** and 128.3° for compound **31** are remarkably similar to those found in Cp'_2TiCl_2[14] and Cp'_2ZrCl_2,[15] (see Table 4.6 for a comparison of structural data) where the corresponding angles are 130.2° and 128.9°, respectively. Some asymmetry is noted in the M-Cl bond lengths, with M-Cl(1)/M-Cl(2) distances of 2.351(3) Å/2.325(4) Å for M = Ti and 2.431(3) Å/2.412(2) Å for M = Zr. The M-Cl(1) distances are similar to the corresponding bond lengths in $Cp_2'TiCl_2$ and Cp'_2ZrCl_2, suggesting that this bond length is normal. We suggest that the somewhat shorter M-Cl(2) distances may be due to intramolecular non-bonded contacts, since the intermolecular contacts are similar for both Cl(1) and Cl(2). However, Cl(2) has additional intramolecular non-bonded contacts with H(5A), H(6B), and H(12A), ranging from 2.75 Å to 2.76 Å, which act in a direction tending to compress the M-Cl(2) distances. The cyclopentadienyl rings are planar, with deviations from the least squares planes of 0.002 Å to 0.01 Å in compound **30**, whereas those of compound **31** are between 0.001 Å and 0.006 Å. Within the cyclopentadienyl rings the C-C bond lengths and angles show little distortion due to the alkyldiphenylphosphino substituent, with the same average C-C bond lengths and angles at the substituted carbon of 1.41 Å and 107° for compounds **30** and **31**. The unsubstituted C-C bond lengths and angles are 1.40 Å/108° for **28** and 1.41 Å/108° for

Table 4.6. A Comparison of Structural Parameters for Cyclopentadienyl(alkyl)diphenylphosphine Complexes[a, c, d]

(a) bond angles.(deg)	Cp'_2TiCl_2[a]	Cp'_2ZrCl_2[a]	Zr (**26**)	MoZr (**A**)[b]	MoTi (**30**)	MoZr (**31**)	RhTi (**32** or **33**)	RhTi (**36**)
Cp(c)-M-Cp(c)	130.2	128.9(2)	130.9	130.2	128.9	128.3	129.7	127.7
P-M'-P				93.69(2)	100.6(1)	100.87(8)	176.05(5)	164.3(1)
Cl-M-Cl	93.15	95.10(5)	99.69	96.69(3)	93.5(1)	96.3(1)	94.21(6)	95.1(2)
(b) bond lengths (Å)								
P_1-P_2				3.717	3.902	3.915	4.655	4.577
Cp(c)-Cp(c)			4.011	4.027	3.808	4.029	3.751	3.750
Cp(c)-M (average)			2.205	2.220	2.080	2.213	2.060	2.061
M-Cl (average)			2.4448(6)	2.420	2.39	2.422	2.379	2.337
M'-CO_{trans} (average)				1.980	1.97	2.00		
M'-CO_{cis} (average)				2.031	2.02	2.03		
M'-P (average)				2.543	2.535	2.540	2.329	2.313

[a] data for $Cp_2'TiCl_2$ and Cp'_2ZrCl_2 taken from references 14 and 15, respectively;[b]data for $[(\eta^5\text{-}C_5H_4PPh_2)_2ZrCl_2Mo(CO)_4]$ (**A**) taken from reference 2g;[c]Zr (**26**) = $[(\eta^5\text{-}C_5H_4CH_2CH_2PPh_2)_2ZrCl_2]$ (**26**); MoTi (**31**) = $[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)_2TiCl_2Mo(CO)_4]$ (**31**), MoZr (**32**) = $[(\mu\text{-}\eta^5\text{:}\eta^1C_5H_4\ CH_2CH_2PPh_2)_2ZrCl_2Mo(CO)_4]$ (**32**); RhTi (**32** or **33**) = $[(\mu\text{-}\eta^5\text{:}\eta 1\text{-}C_5H_4CH_2CH_2PPh_2)TiCl_2RhCl(CO)]_2$ (32 or 33) RhTi (**36**) = $[(\mu\text{-}\eta^5\text{:}\eta 1\text{-}C_5H_4CH_2PPh_2)TiCl_2RhCl(CO)]_2$ (**36**); M = Ti or Zr, M' = Mo or Rh.

compound **31**. However, the M-C bond lengths show some distortion, presumably due to the presence of the alkyldiphenylphosphino substituent, with the longest bond being to the cyclopentadienyl carbon connected to this substituent, for M = Ti these distances are Ti-C(14) = 2.43(1) and Ti-C(7) = 2.49(1) Å whereas the Ti-C distance for the unsubstituted carbons ranges from 2.33(1) Å to 2.43(1) Å. These metal-carbon separations decrease with distance from the alkyl substituent suggesting that the alkylphosphino group is forcing the Cp rings apart. The structure of **31** shows similar effects in the Zr-Cp carbon bond lengths, and these deviations have also been observed in the crystal structure of $[(\eta^5\text{-}C_5H_4PPh_2)_2ZrCl_2Mo(CO)_4]$(**C**).[8g] About molybdenum, the geometry is pseudooctahedral, with significant distortions due to the presence of the two cis phosphine substituents, which result in a P-Mo-P angle of 100.87(8)° in compound **30**, and a similar value of 100.6(1)° for compound **31**. The large P-M-P angles result in a corresponding decrease of the C(1)-Mo-C(4) bond angle to 84.0(5)° and 83.3(4)° for compounds **30** and **31**, respectively. These distortions were not observed in compound **C**, and are likely due to the preference of the alkylphosphino arms of the metalloligand $[(\eta^5\text{-}C_5H_4CH_2CH_2PPh_2)_2MCl_2]$ (M = Ti (**25**), Zr (**26**)) to be as far apart as possible, as was evidenced by the solid-state structure of compound **26** (*vide supra*). The bending back of the carbonyls cis to the phosphine units (with C(1)-Mo-C(4) bond angles of 173.6(5)° in **30** and 173.8(4)° in **31**) has also been observed in compound **C**, and in $[(dppm)Mo(CO)_4]$,[16] where the corresponding angles are 169° and 168°, respectively, and these may arise from steric interactions with the phosphorus-bound phenyl rings. Although one would expect a trans influence in the Mo-C bond lengths, with those trans to the phosphines shorter than those trans to the strongly π-acidic carbonyls due to competition for π-electron density, there is no obvious correlation for reasons that are not clear. Due to the orientations of the methylene groups, in which one hydrogen from each is pointing into the pocket between Zr and Mo, there is very little access between the metals. This is shown clearly in the space-filling diagrams of compound **31** in Figures 4.1.2 and 4.1.3, in which the first shows the view from the side of $ZrCl_2$ face, and the second shows the view from the opposite side. Although it is not obvious from the "ball and stick" drawings in Figures 4.1 and 4.1.1, Figure 4.1.2 shows that the phenyl groups on the phosphine end of the bridging ligand also block access to the Mo center on the side adjacent to the $ZrCl_2$ moiety. However it is also evident from Figures 4.1.2 and 4.1.3 that approach to the zirconium-bound halides is uninhibited, as is the approach at Mo remote from the $ZrCl_2$ moiety. Attempts to thermally induce the isomerization of the phosphine groups from a cis to a trans arrangement were unsuccessful, and resulted in significant amounts of decomposition. Similarily, a convenient mononuclear Mo synthon, having labile groups in a trans orientation was not available for the direct synthesis of a M/Mo compound (M = Ti, Zr) having a trans phosphine arrangement.

Since the cis-phosphine orientation in compounds **30** and **31** results in a large metal-metal separation, we decided to look at late-metal sources in which the phosphines would be expected to bind in a mutually trans arrangement. Initial attempts at obtaining a group 4 metal-rhodium combination were unsuccessful, with the addition of $[RhCl(CO)_2]_2$ to $[(\eta^5\text{-}C_5H_4CH_2CH_2PPh_2)_2TiCl_2]$ (**25**) or the reverse, under a variety of conditions, resulting in the formation of a large number of products. If however, THF solutions of **25** and $[RhCl(CO)_2]_2$ are simultaneously and slowly added to THF at low temperature, two compounds, "α"-$[(\mu\text{-}\eta^5\text{-}C_5H_4CH_2CH_2PPh_2)_2TiCl_2RhCl(CO)]_2$ (**32a**) and "β"-$[(\mu\text{-}\eta^5\text{-}C_5H_4CH_2CH_2PPh_2)_2TiCl_2RhCl(CO)]_2$ (**32b**) are obtained as shown in Scheme 4.1, where α and β are clearly isomers. Compound **32a** could be obtained pure via a careful recrystallization of the reaction mixture. This compound has a doublet in the $^{31}P\{^1H\}$ NMR spectrum at 26.3 ppm with 124 Hz coupling to Rh, and shows AA'BB'

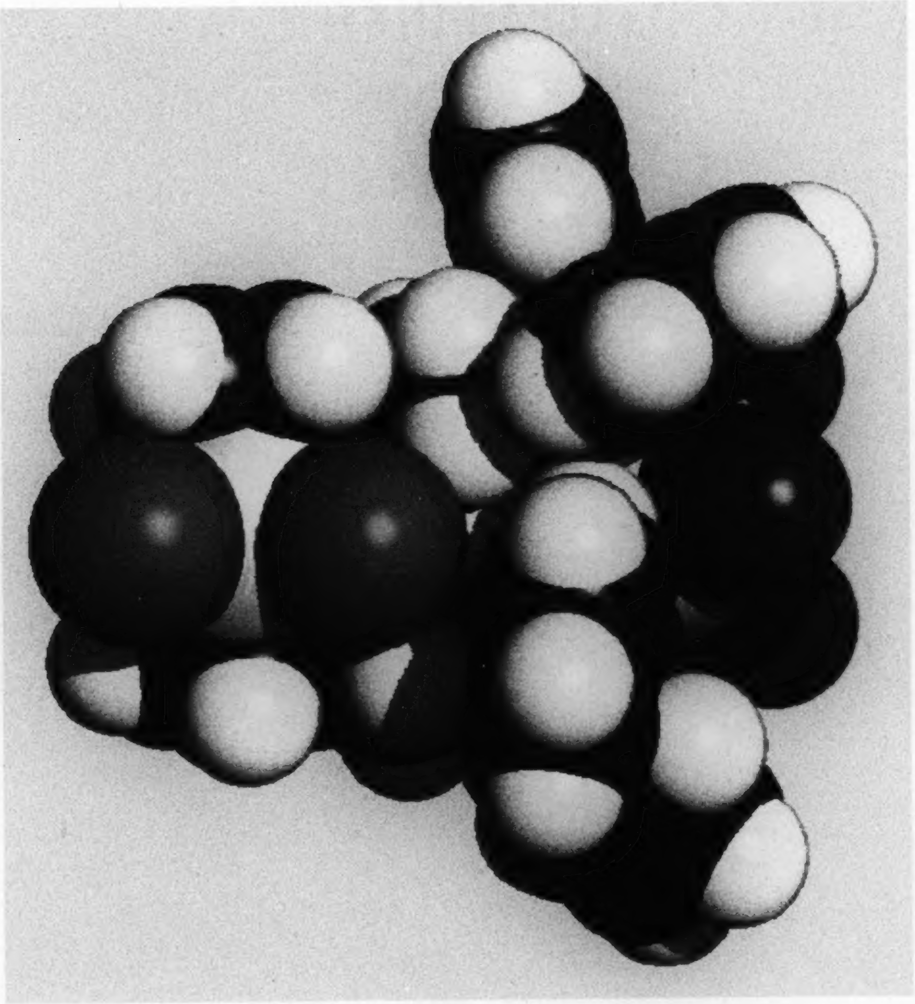


Figure 4.1.2. Space filling depiction of compound **31** showing access to the zirconium-bound chlorides. The orientation shown is the same as that shown in Figure 4.1.

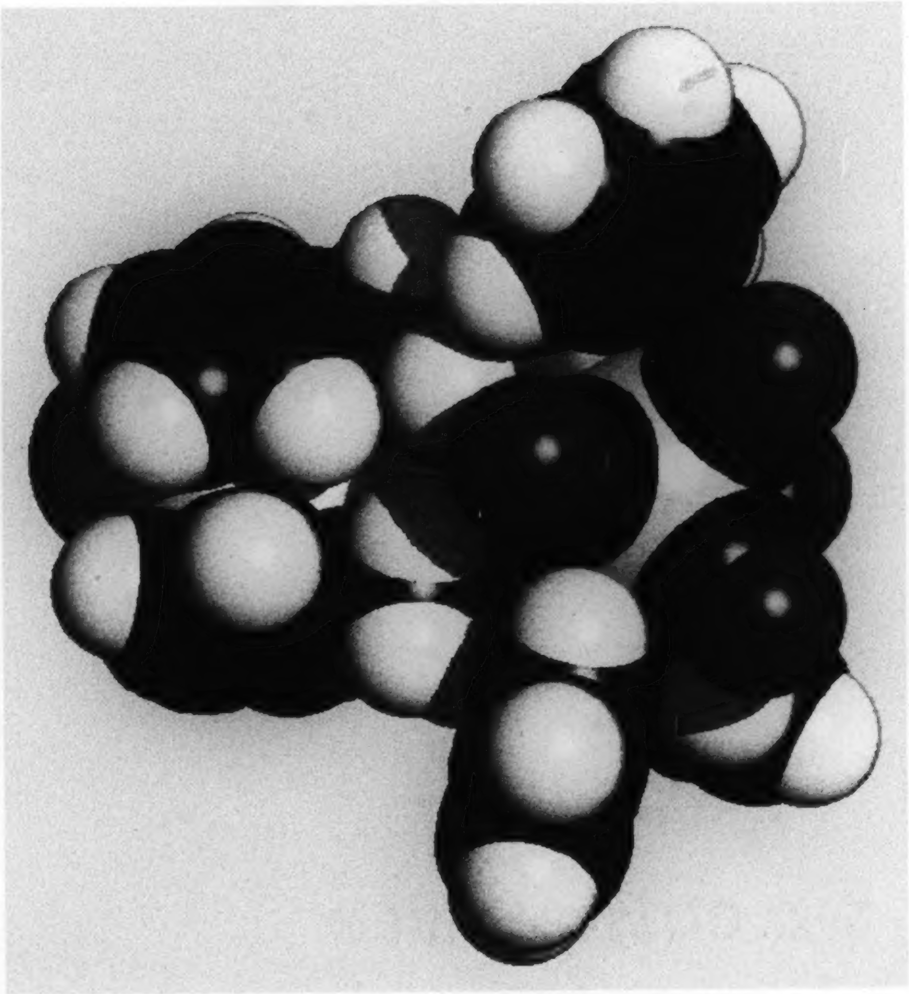
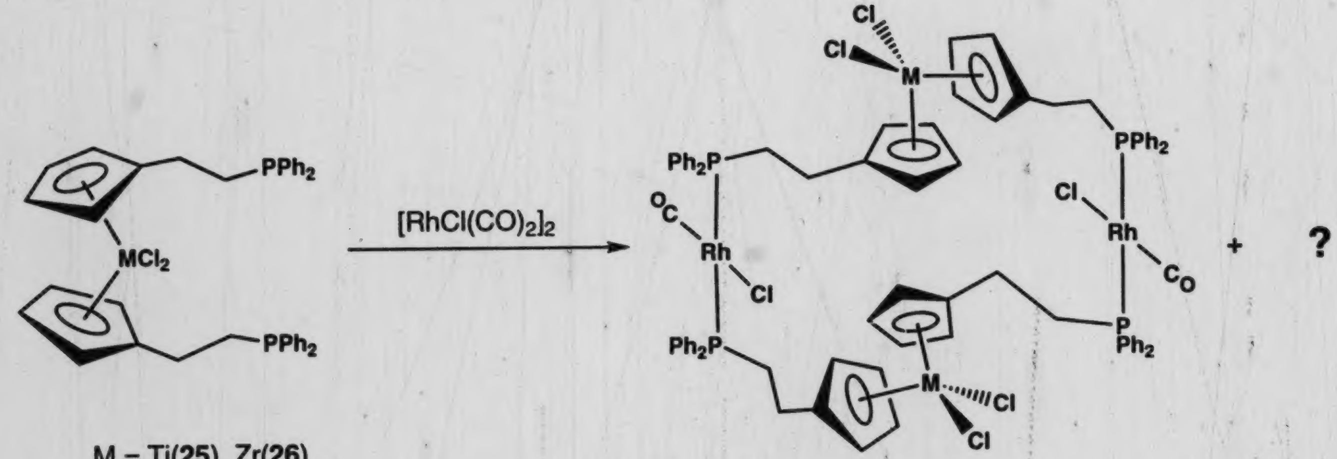


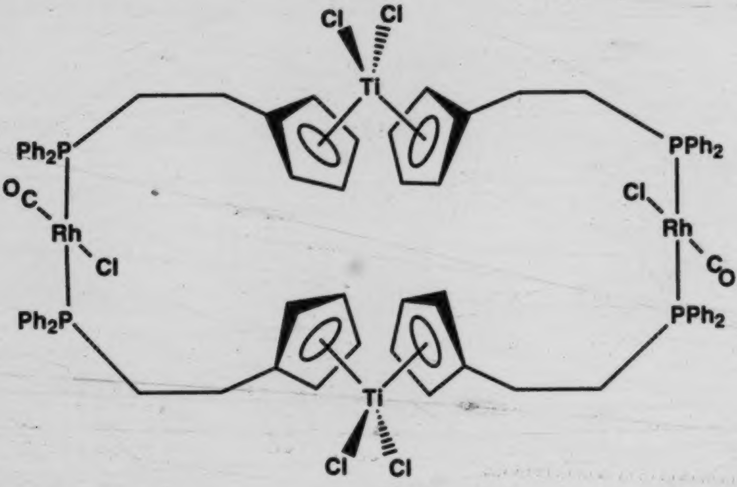
Figure 4.1.3. Space filling depiction of compound **31** showing access to the molybdenum center.

Scheme 4.1. Preparation of $[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)MCl_2RhCl(CO)]_2$

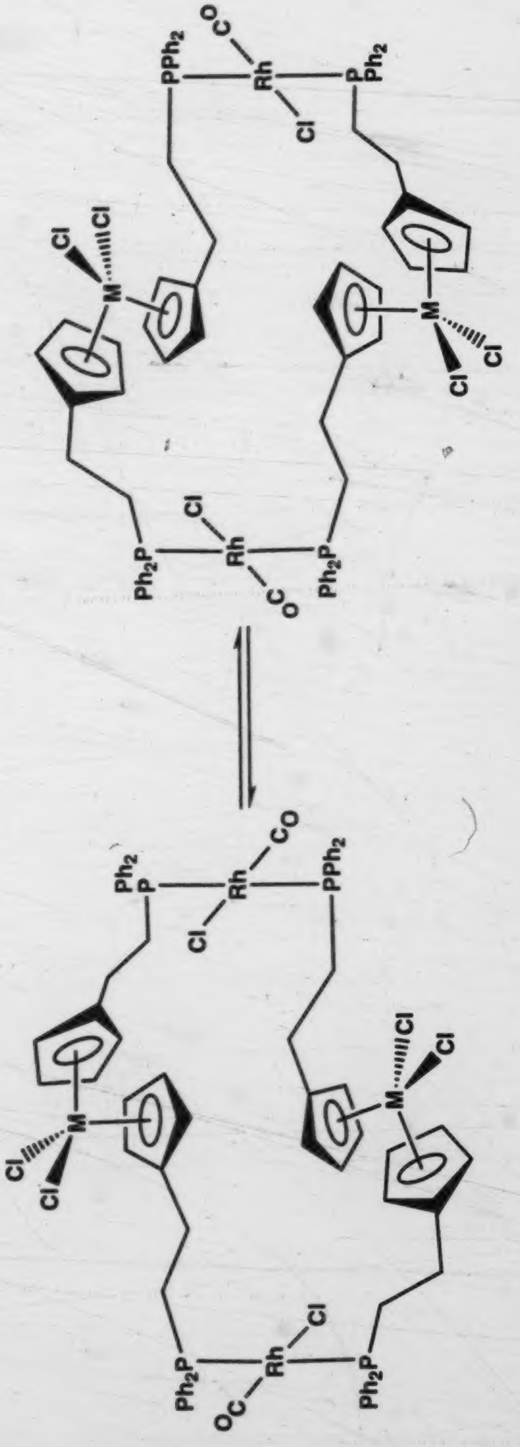

PPh2
MCl2
PPh2
[RhCl(CO)2]2
Cl
Cl
M
Ph2P
OC
Rh
Cl
Ph2P
PPh2
Cl
Rh
CO
P
Ph2
M
Cl
Cl
+
?

M = Ti(**25**), Zr(**26**)

M = Ti (**32a** or **b**), Zr (**33a** or **b**) resonances centered at 6.38 ppm in the ^{1}H NMR, with the two methylene resonances at 3.10 and 2.94 ppm appearing as complex multiplets. ^{13}C{^{1}H} NMR spectroscopy shows a terminally-bound carbonyl ligand resonating at 188.1 ppm with 75.6 Hz rhodium coupling and 14.3 Hz coupling to the two rhodium-bound phosphines. Compound **32a** slowly converts to a *ca.* 2:1 mixture of **32a** and **b** over several days. Compound **32b** has a doublet at 31.2 ppm in the ^{31}P{^{1}H} NMR spectrum with 127 Hz Rh-coupling, with the carbonyl carbon resonance obscured by that of **32a** in the ^{13}C NMR spectrum. The ^{1}H NMR spectrum of this compound differs in that there is apparent asymmetry in the molecule, as each Cp hydrogen resonates at a different chemical shift, suggesting that either the front and back of the $P_4Rh_2Ti_2$ plane are in different chemical environments or there are two sets of chemically equivalent Cp rings, as will be discussed in detail later. The IR spectra of pure **32a** and a mixture of compounds **32a** and **32b** are identical, each with a terminal carbonyl band at 1976 cm^{-1}. It was not known if the compounds contained two or four metals and the extremely low solubility of these compounds precluded molecular weight determinations, so they were analyzed by electrospray mass spectroscopy. The mass spectrum of **32a** showed a number of signals around m/z = 1644, which corresponds to an molecular ion peak for M - Cl if the compound contains four metals. By comparison, the mass spectrum of $[(\mu\text{-}\eta^5\text{-}C_5H_4CH_2PPh_2)_2\text{-}TiCl_2RhCl(CO)]_2$ (**34**), which had been characterized crystallographically (*vide infra*), was obtained and also showed a molecular-ion peak at an m/z corresponding to M - Cl. Both of these spectra were identical to the calculated spectra for the expected isotopic pattern for a compound containing two Ti and two Rh atoms, indicating that compound **32a** is dimeric in nature. The mass spectrum of a mixture of compounds **32a** and **32b** is exactly the same as that of pure **32a**, which suggests that both compounds are isomers. A single crystal suitable for X-ray diffraction was obtained from a mixture of **32a** and **b**, but it was not known which isomer the crystal corresponded to, and an NMR spectrum of the remaining solid from the crystallization showed the presence of both **32a** and **b**. See Table 4.7 for selected bond lengths and angles. Inspection of the structure, shown in Figure 4.2 indicates that in the ^{1}H NMR spectrum there should be four Cp hydrogen chemical environments, if the molecule retains this orientation in solution, as the Cp rings pointing out of the cavity are chemically distinct from those directed into the cavity. This may indicate that the crystal obtained corresponds to compound **32b** and that compound **32a** may have a structure with higher symmetry, like that shown below.



This orientation results in a symmetric Cp environment, and could account for the AA'BB' pattern in the Cp region of the ^{1}H NMR spectrum. Another possibility is that the X-ray structure shown in Figure 4.2 corresponds to compound **32a** and in solution fluxional processes equilibrate the Cp hydrogen environments, as shown in Scheme 4.2. If, as suggested above, the crystal structure is of **32a**, with a facile interchange of Cp ring positions, then the question arises about the nature of the isomerism between compounds **32a** and **b**, since this fluxional process would seem to rule out structures related by


Ph2P
Rh
Cl
OC
Ph2P
M
Cl
Cl
Ph2
P
Rh
CO
PPh2
Cl
M
Cl
Cl
PPh2
Rh
CO
Cl
P
Ph2
M
Cl
Cl
Ph2P
Rh
Cl
OC
Ph2P
M
Cl
Cl

Scheme 4.2

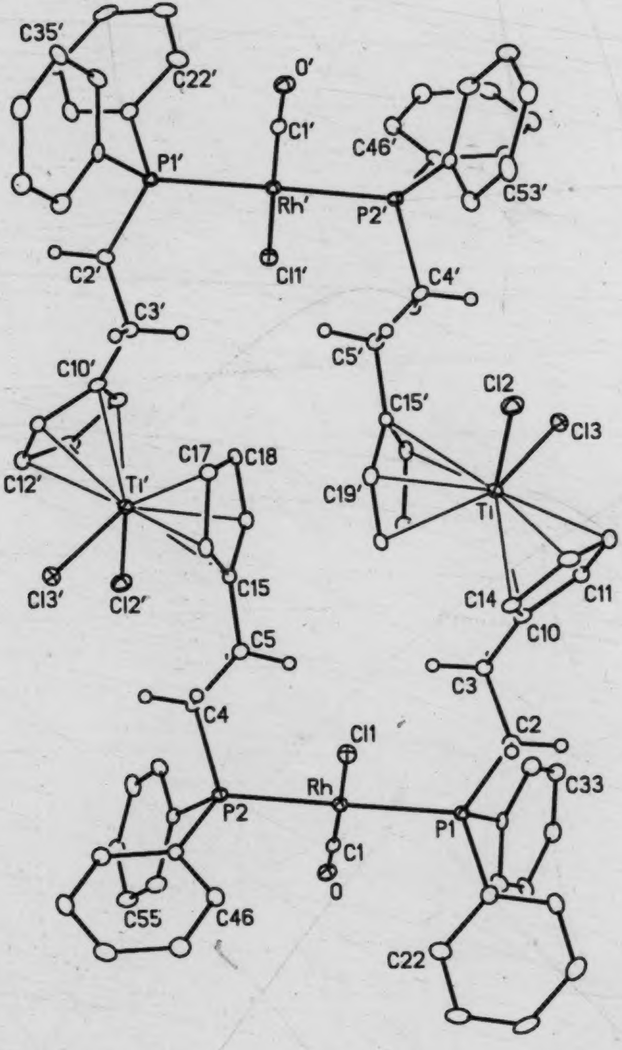

C35′
C22′
O′
C1′
C46′
P1′
Rh′
P2′
C53′
C2′
Cl1′
C4′
C3′
C5′
C10′
Cl2
C15′
Cl3
C17
C18
C12′
Ti′
C19′
Ti
Cl3′
Cl2′
C15
C14
C11
C10
C5
C3
C4
C2
Cl1
Rh
C33
P2
P1
C1
O
C55
C46
C22

Figure 4.2. Perspective view of the $[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)_2TiCl_2RhCl(CO)]_2$ **(32)** molecule showing the atom labelling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters for the methylene groups, and are not shown for the η^5–C_5H_4 or phenyl groups. Primed atoms are related to unprimed ones via the crystallographic inversion center at (1/4, 1/4, 1/2).

Table 4.7 Selected Bond Lengths and Angles for Compound 32

(a) Selected Interatomic Distances (Å)

Atom1	Atom2	Distance
Rh	Cl(1)	2.3830(14)
Rh	P(1)	2.336(2)
Rh	P(2)	2.322(2)
Rh	C(1)	1.816(6)
Ti	Cl(2)	2.382(2)
Ti	Cl(3)	2.375(2)
Ti	C(10)	2.435(5)
Ti	C(11)	2.374(5)
Ti	C(12)	2.321(6)
Ti	C(13)	2.377(5)
Ti	C(14)	2.378(5)
Ti	C(15')	2.465(5)
Ti	C(16')	2.414(5)
Ti	C(17')	2.331(5)
Ti	C(18')	2.348(5)
Ti	C(19')	2.393(6)
P(1)	C(2)	1.839(5)
P(1)	C(21)	1.838(5)
P(1)	C(31)	1.839(6)
P(2)	C(4)	1.857(5)
P(2)	C(41)	1.837(5)
P(2)	C(51)	1.822(5)
O	C(1)	1.148(6)
C(2)	C(3)	1.541(7)
C(3)	C(10)	1.507(7)
C(4)	C(5)	1.527(7)
C(5)	C(15)	1.501(7)
C(10)	C(11)	1.403(7)
C(10)	C(14)	1.418(7)
C(11)	C(12)	1.406(7)
C(12)	C(13)	1.384(8)
C(13)	C(14)	1.421(7)
C(15)	C(16)	1.402(7)
C(15)	C(19)	1.423(7)
C(16)	C(17)	1.419(7)
C(17)	C(18)	1.412(7)
C(18)	C(19)	1.416(7)

Primed atoms are related to unprimed ones via the inversion center at ($^{1}/_{4}$, $^{1}/_{4}$, $^{1}/_{2}$).

(b) Selected Interatomic Angles (deg)

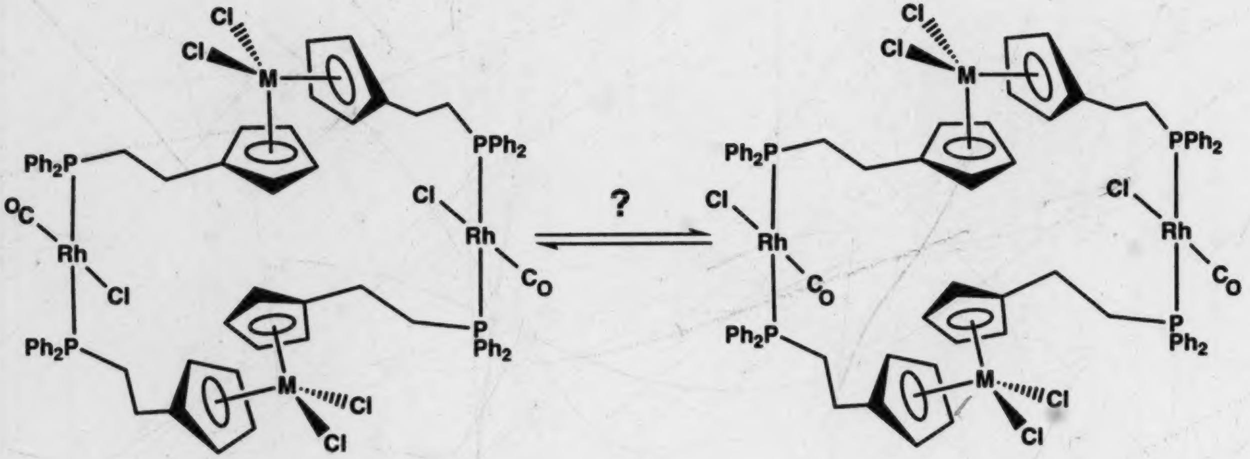
Atom1	Atom2	Atom3	Angle
Cl(1)	Rh	P(1)	88.75(5)
Cl(1)	Rh	P(2)	87.44(5)
Cl(1)	Rh	C(1)	176.6(2)
P(1)	Rh	P(2)	176.05(5)
P(1)	Rh	C(1)	92.1(2)
P(2)	Rh	C(1)	91.6(2)
Cl(2)	Ti	Cl(3)	94.21(6)
Rh	P(1)	C(2)	116.1(2)
Rh	P(1)	C(21)	108.3(2)
Rh	P(1)	C(31)	118.5(2)
C(2)	P(1)	C(21)	103.3(2)
C(2)	P(1)	C(31)	104.9(3)
C(21)	P(1)	C(31)	104.0(2)
Rh	P(2)	C(4)	110.6(2)
Rh	P(2)	C(41)	115.1(2)
Rh	P(2)	C(51)	117.2(2)
C(4)	P(2)	C(41)	105.0(2)
C(4)	P(2)	C(51)	105.9(2)
C(41)	P(2)	C(51)	101.9(2)
Rh	C(1)	O	176.4(5)
P(1)	C(2)	C(3)	115.9(4)
C(2)	C(3)	C(10)	109.1(4)
P(2)	C(4)	C(5)	111.7(4)
C(4)	C(5)	C(15)	115.1(5)
C(3)	C(10)	C(11)	126.7(5)
C(3)	C(10)	C(14)	125.9(5)

Table 4.7 (cont.)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C(11)	C(10)	C(14)	107.1(5)	C(17)	C(18)	C(19)	107.2(4)
C(10)	C(11)	C(12)	108.2(5)	C(15)	C(19)	C(18)	109.0(5)
C(11)	C(12)	C(13)	109.1(5)	P(1)	C(21)	C(22)	118.3(4)
C(12)	C(13)	C(14)	107.4(5)	P(1)	C(21)	C(26)	123.4(4)
C(10)	C(14)	C(13)	108.1(5)	P(1)	C(31)	C(32)	122.0(4)
C(5)	C(15)	C(16)	127.8(5)	P(1)	C(31)	C(36)	119.7(4)
C(5)	C(15)	C(19)	125.3(5)	P(2)	C(41)	C(42)	121.0(4)
C(16)	C(15)	C(19)	106.8(4)	P(2)	C(41)	C(46)	120.3(4)
C(15)	C(16)	C(17)	109.0(5)	P(2)	C(51)	C(52)	122.0(4)
C(16)	C(17)	C(18)	108.0(5)	P(2)	C(51)	C(56)	120.5(4)

different orientations of the Cp_2TiCl_2 moieties. One possibility is that compound **32b** results from exchange of the carbonyl and halide ligands from an arrangement as in **32a**, where they are mutually anti on adjacent rhodium centers, to one in which they are in a syn arrangement about these metals, as is indicated in Scheme 4.3. This suggestion seems less likely though, as the significant difference in ^{31}P NMR chemical shifts of 4.9 ppm in compounds **32a** and **32b** would not be expected. Accordingly, we currently favour the former explanation. We had also considered that the tetranuclear species could be slowly generating two equivalents of a binuclear RhTi complex, in which the trans arrangement of the chloride and carbonyl ligands about rhodium renders the front and back faces of the P_2RhTi framework inequivalent in the ^1H NMR spectrum. However this formulation is not supported by the mass spectral data. The X-ray structure of $[(\mu\text{-}\eta^5\text{-}C_5H_4CH_2CH_2\text{-}PPh_2)_2TiCl_2RhCl(CO)]_2$ (**32a** or **b**) showed that the compound crystallized in the C2/c space group (No. 15), and was found to sit on an inversion center, therefore 1/2 of the molecule is related by inversion symmetry to the other. The structure, shown in Figure 4.2, confirms that the complex is tetranuclear, containing two rhodium and two titanium atoms. This complex contains two *trans*-$[RhCl(CO)P_2]$ units, bridged by the two diphosphine metalloligands and as such, resembles the large number of reported diphosphine-bridged binuclear compounds.[17] The substituted cyclopentadienyl groups are staggered, with a head to tail arrangement of these ligands, with each phosphine of the metalloligand aimed in opposite directions with respect to the $TiCl_2$ moiety and bound to a different rhodium center. The $TiCl_2$ fragments are also aimed away from each other, and are directed towards the outside of the cavity formed by the $Rh_2Ti_2P_4$ framework. The macrocyclic structure results in a large separation between metals, with a Rh-Rh' separation of 11.875 Å, a Ti-Ti' distance of 7.345 Å and an average RhTi separation of 6.891 Å. About titanium, the geometry is pseudotetrahedral, as is typically observed for

Scheme 4.3


Cl
Cl
M
Ph2P
PPh2
OC
Rh
Cl
Cl
Rh
CO
Ph2P
P
Ph2
M
Cl
Cl
?

M = Ti (32a), Zr (33a)

M = Ti (32b), Zr (33b)

metallocene dichlorides. See Table 4.6 for a comparison of these values. The average Cp(centroid)-Ti, Ti-Cl bond lengths of 2.060 Å and 2.379 Å, respectively, and the Cp(centroid)-Ti-Cp(centroid) angle of 129.7° are normal, and as was noted for [*cis*-(μ-η^5-$C_5H_4CH_2CH_2PPh_2)_2TiCl_2Mo(CO)_4$] (**30**), are remarkably similar to the corresponding values in Cp'_2TiCl_2. One cyclopentadienyl ring on each of the titanium centers is directed into the $Rh_2Ti_2P_4$ cavity, with the Cp rings on adjacent Ti atoms *ca.* 3.2 Å apart. Figure 4.2.1 clearly shows a π-stacking interaction[18] of these groups, and their separation is somewhat less than the predicted van der Waals separation of ca. 3.40 Å[19] Although the view shown in Figure 4.2 gives the impression of open space between the metals, the very short Cp-Cp separation effectively cuts the cavity in two and the methylene hydrogens which point inward block the half cavities. This is shown by the non-bonded hydrogen-hydrogen contacts across the cavity for H(3B)-H(5A) of 2.83 Å and between this hydrogen and the phosphorus-bound or cyclopentadienyl-bound hydrogens H(3B)-H(17') of 2.40 Å, and H(3B)-H(18') of 2.26 Å, respectively and the H(3B)-Cl(1) contact of 2.77 Å, where H(3B) is the C(3)-bound hydrogen that is pointing into the cavity. Figure 4.2.1 shows a space filling diagram for this compound, and from this view, the π-stacking is evident. This figure suggests that a fluxional process that exchanges the positions of the Cp rings should not be facile and seems therefore to rule out the possibility suggested earlier that the X-ray structure is that of isomer **32a**. It is also evident from Figure 4.2.1 that there is apparent access to the rhodium centers. The potential accessibility to the vacant rhodium sites is supported in the alternate view of the complex shown in Figure 4.2.2, in which only the ipso carbons on the phenyl rings are shown. Access from within the macrocycle seems possible since it is only partially blocked by the methylene hydrogens in the C_2H_4 linker, and access from the outside of the macrocyclic ring also appears to be possible, suggesting the potential for reactivity to

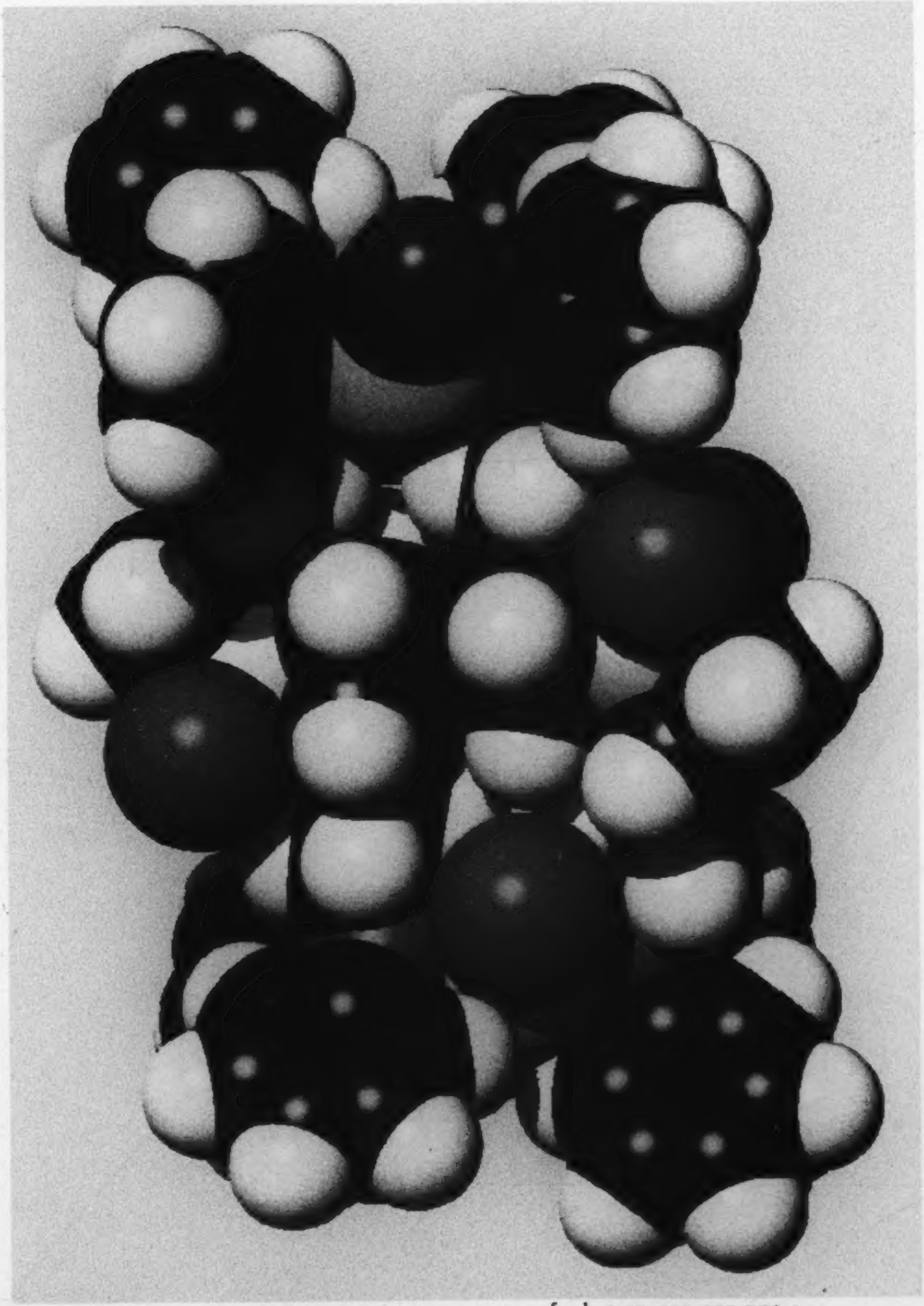


Figure 4.2.1. Space filling depiction of $[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)_2\text{-}TiCl_2RhCl(CO)]_2$ (**32**). The orientation is the same as that of Figure 4.2.

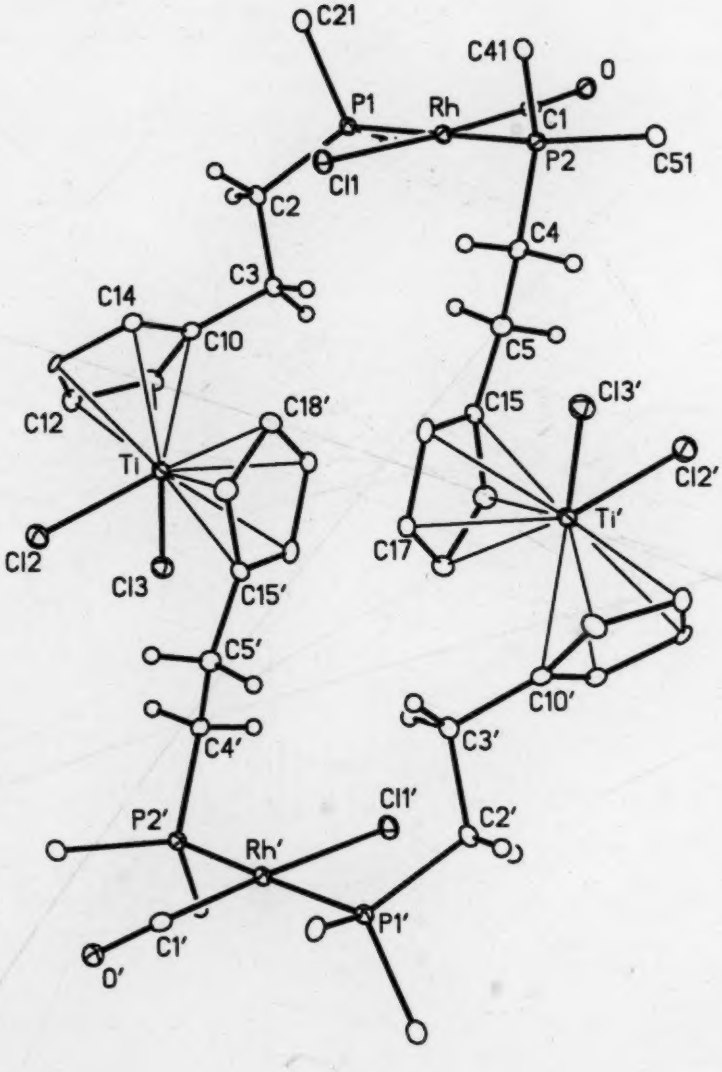

C21
C41
O
P1
Rh
C1
P2
C51
Cl1
C2
C4
C3
C14
C10
C5
C15
Cl3'
C12
C18'
Ti
Cl2'
Ti'
C17
Cl2
Cl3
C15'
C5'
C10'
C3'
C4'
Cl1'
C2'
P2'
Rh'
P1'
C1'
O'

Figure 4.2.2 Alternate view of compound **32** showing access to the rhodium centers.

occur at these sites. In this structure, the $TiCl_2$ units are more hindered than in the Ti/Mo analogue, [*cis*-(μ-η^5-$C_5H_4CH_2CH_2PPh_2)_2TiCl_2Mo(CO)_4$] (**30**), with the phosphorus-bound phenyl groups blocking access to the titanium center. About rhodium, the geometry closely resembles that found in the dppm-bridged complex, *trans*-[$Rh_2Cl_2(CO)_2$(dppm)$_2$] (**D**),[17a] with square planar ligand arrangements about this metal. The average Rh-P bond lengths and P-Rh-P bond angles of 2.329 Å and 176.05° are similar to those found in compound **D**, as are the Rh-Cl (2.383(1) Å) and the Rh-C (1.816(6) Å) bond lengths. The chloride and carbonyl ligands are bent slightly away from the $Rh_2Ti_2P_4$ cavity, with a Cl-Rh-C bond angle of 176.6(2) °, and this bending is likely due to steric interactions between these ligands and substituents inside the cavity. The complex α-[(μ-η^5-$C_5H_4CH_2CH_2PPh_2)_2ZrCl_2RhCl(CO)]_2$ (**33a**) was prepared similarily and had a ^{31}P NMR chemical shift of 26.0 ppm with a rhodium-phosphorus coupling of 125.7 Hz. This species displays an AA'BB' pattern for the Cp hydrogens in the ^1H NMR spectrum centered at 6.27 ppm, suggesting that the compound has a similar structure to the titanium-containing analogue, α-[(μ-η^5-$C_5H_4CH_2CH_2PPh_2)_2TiCl_2$-$RhCl(CO)]_2$ (**32a**). After three days in solution, partial isomerization of **33a** had taken place, generating the isomer, β-[(μ-η^5-$C_5H_4CH_2CH_2PPh_2)_2ZrCl_2$-$RhCl(CO)]_2$ **33b**, (δ ^{31}P = 30.6 ppm, $^1J_{Rh\text{-}P}$ = 126.7 Hz). The Cp region of the ^1H NMR spectrum of **33b** suggests that it possesses a structure similar to the titanium analogue, compound **32b**.

In order to determine the types of products obtained when metallocene-dichloride derivatives having a one-carbon spacer between the Cp and PPh_2 units were reacted with late-metal sources, the reactivities of [η^5-$C_5H_4CH_2PPh_2)_2MCl_2$] M = Ti (**27**), Zr (**28**) were studied. In contrast to the above, addition of two equivalents of [(η^5-C_5H_4-$CH_2PPh_2)_2TiCl_2$] (**27**) to $[RhCl(CO)_2]_2$ in THF results in the formation of a single compound, [(μ-η^5-$C_5H_4CH_2PPh_2)_2TiCl_2RhCl(CO)]_2$ (**34**). No isomerization occurs upon standing in solution for days. The $^{31}P\{^1H\}$ NMR spectrum of this compound shows a doublet at 32.1 ppm with 125.7 Hz rhodium coupling. ^1H NMR spectroscopy shows the compound possesses front-back symmetry, with the cyclopentadienyl AA'BB' resonance centered at 6.57 ppm. In this compound, the methylene resonance appears as a psuedotriplet at 3.99 ppm with $^2J_{PH} = {}^4J_{PH} = 3.5$ Hz. The equivalence of the two- and four-bond couplings has been observed in similar compounds[8c] and has been attributed to virtual coupling.[20] The $^{13}C\{^1H\}$ NMR spectrum of this compound shows a carbonyl resonance at 185.7 ppm, appearing as a doublet of triplets. Coupling to two equivalent rhodium-bound phosphines gives rise to a triplet with a coupling constant of 15.4 Hz and the rhodium coupling of 74.5 Hz indicates the carbonyl is terminally bound to this metal. IR spectroscopy on this compound shows a band for this terminal carbonyl at 1973 cm^{-1}. A molecular weight determination on this compound suggested that, similar to the species described above, $[(\mu\text{-}\eta^5\text{-}C_5H_4CH_2CH_2PPh_2)_2TiCl_2RhCl(CO)]_2$ (**32a** and **32b**), the complex contained two titanium and two rhodium atoms. To confirm the tetranuclear structure, and to determine the structural differences that would result from changing the bridging ligand to one containing a one-carbon spacer, the compound was analyzed by X-ray crystallography. The structure, shown in Figure 4.3, verifies a macrocyclic tetranuclear formulation. Selected bond lengths and angles are given in Table 4.8. The presence of one less carbon in the bridging ligand when compared to $[(\mu\text{-}\eta^5\text{-}C_5H_4CH_2CH_2PPh_2)_2TiCl_2RhCl(CO)]_2$ (**32**) has resulted in a shorter Rh-Rh separation of 9.009 Å, and a Ti-Ti separation of 8.246 Å, while the analogous values in compound **32** are 11.875 Å and 7.345 Å. The average Rh-Ti distance of 6.113 Å in compound **34** is shorter than that found in compound **32**, and is also a result of the shorter alkyl spacer between the cyclopentadienyl and phosphine units in the bridging ligand. The longer Ti-Ti distance in this complex is due to the orientation of the cyclopentadienyl rings, where

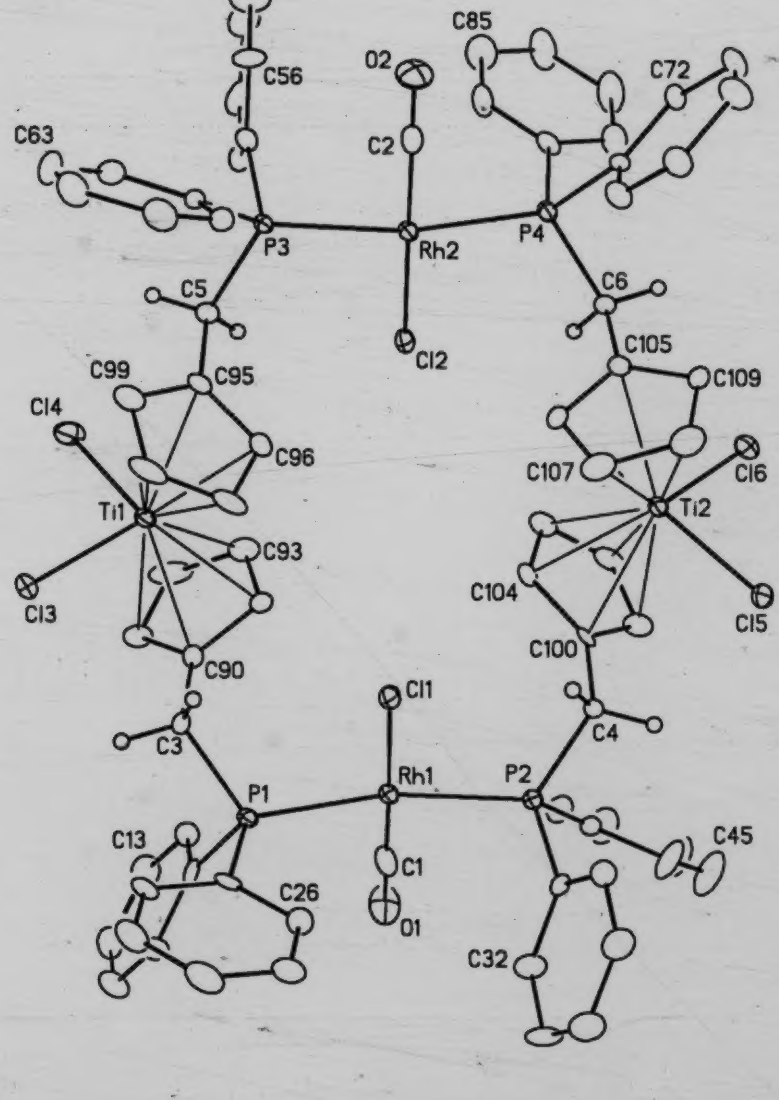

C85
C72
O2
C56
C63
C2
P3
Rh2
P4
C5
C6
Cl2
C105
C99
C95
C109
Cl4
C96
C107
Cl6
Ti1
Ti2
C93
C104
Cl3
Cl5
C100
C90
Cl1
C3
C4
Rh1
P1
P2
C13
C45
C1
C26
O1
C32

Figure 4.3. Perspective view of the $[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4CH_2PPh_2)_2TiCl_2RhCl(CO)]_2$ (**34**) molecule showing the atom labelling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters for the methylene groups, and are not shown for the PPh_2 phenyl groups and the titanium-bound cyclopentadienyl groups.

Table 4.8 Selected Bond Lengths and Angles for Compound 34

(a) Selected Interatomic Distances (Å)

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Rh(1)	Cl(1)	2.395(3)	P(1)	C(3)	1.852(11)
Rh(1)	P(1)	2.309(3)	P(1)	C(11)	1.824(13)
Rh(1)	P(2)	2.306(3)	P(1)	C(21)	1.830(11)
Rh(1)	C(1)	1.74(2)	P(2)	C(4)	1.834(11)
Rh(2)	Cl(2)	2.378(3)	P(2)	C(31)	1.827(11)
Rh(2)	P(3)	2.317(3)	P(2)	C(41)	1.797(13)
Rh(2)	P(4)	2.318(3)	P(3)	C(5)	1.847(11)
Rh(2)	C(2)	1.785(14)	P(3)	C(51)	1.824(12)
Ti(1)	Cl(3)	2.339(4)	P(3)	C(61)	1.827(14)
Ti(1)	Cl(4)	2.338(4)	P(4)	C(6)	1.857(10)
Ti(1)	C(90)	2.391(11)	P(4)	C(71)	1.830(12)
Ti(1)	C(91)	2.400(12)	P(4)	C(81)	1.825(11)
Ti(1)	C(92)	2.376(14)	O(1)	C(1)	1.20(2)
Ti(1)	C(93)	2.329(15)	O(2)	C(2)	1.160(15)
Ti(1)	C(94)	2.383(12)	C(3)	C(90)	1.492(14)
Ti(1)	C(95)	2.403(11)	C(4)	C(100)	1.518(14)
Ti(1)	C(96)	2.354(11)	C(5)	C(95)	1.519(14)
Ti(1)	C(97)	2.297(12)	C(6)	C(105)	1.499(14)
Ti(1)	C(98)	2.400(12)	C(90)	C(91)	1.432(15)
Ti(1)	C(99)	2.420(13)	C(90)	C(94)	1.42(2)
Ti(2)	Cl(5)	2.343(4)	C(91)	C(92)	1.39(2)
Ti(2)	Cl(6)	2.327(4)	C(92)	C(93)	1.40(2)
Ti(2)	C(100)	2.416(10)	C(93)	C(94)	1.41(2)
Ti(2)	C(101)	2.406(12)	C(95)	C(96)	1.40(2)
Ti(2)	C(102)	2.409(13)	C(95)	C(99)	1.41(2)
Ti(2)	C(103)	2.352(13)	C(96)	C(97)	1.41(2)
Ti(2)	C(104)	2.384(11)	C(97)	C(98)	1.42(2)
Ti(2)	C(105)	2.386(11)	C(98)	C(99)	1.41(2)
Ti(2)	C(106)	2.385(11)	C(100)	C(101)	1.42(2)
Ti(2)	C(107)	2.331(13)	C(100)	C(104)	1.39(2)
Ti(2)	C(108)	2.405(14)	C(101)	C(102)	1.39(2)
Ti(2)	C(109)	2.422(12)	C(102)	C(103)	1.42(2)

Table 4.8 (cont.)

Atom1	Atom2	Distance	Atom1	Atom2	Distance
C(103)	C(104)	1.40(2)	C(106)	C(107)	1.40(2)
C(105)	C(106)	1.40(2)	C(107)	C(108)	1.42(2)
C(105)	C(109)	1.41(2)	C(108)	C(109)	1.42(2)

(b) nonbonded distances

Rh(1)	Rh(2)	9.009(2)	P(2)	P(4)	9.440(5)
Ti(1)	Ti(2)	8.246(4)	H(94)	H(104)	2.713
P(1)	P(3)	9.455(4)	H(96)	H(106)	2.897

(c) Selected Interatomic Angles (deg)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
Cl(1)	Rh(1)	P(1)	89.09(11)	Rh(1)	P(2)	C(41)	123.2(4)
Cl(1)	Rh(1)	P(2)	89.60(11)	C(4)	P(2)	C(31)	102.9(5)
Cl(1)	Rh(1)	C(1)	178.9(5)	C(4)	P(2)	C(41)	100.9(5)
P(1)	Rh(1)	P(2)	164.31(11)	C(31)	P(2)	C(41)	103.6(5)
P(1)	Rh(1)	C(1)	89.8(5)	Rh(2)	P(3)	C(5)	118.2(4)
P(2)	Rh(1)	C(1)	91.4(4)	Rh(2)	P(3)	C(51)	102.9(4)
Cl(2)	Rh(2)	P(3)	90.73(11)	Rh(2)	P(3)	C(61)	123.4(4)
Cl(2)	Rh(2)	P(4)	88.71(11)	C(5)	P(3)	C(51)	104.5(5)
Cl(2)	Rh(2)	C(2)	177.1(4)	C(5)	P(3)	C(61)	100.4(5)
P(3)	Rh(2)	P(4)	162.72(11)	C(51)	P(3)	C(61)	105.5(6)
P(3)	Rh(2)	C(2)	89.7(4)	Rh(2)	P(4)	C(6)	116.7(4)
P(4)	Rh(2)	C(2)	90.0(4)	Rh(2)	P(4)	C(71)	117.4(4)
Cl(3)	Ti(1)	Cl(4)	95.1(2)	Rh(2)	P(4)	C(81)	107.5(4)
Cl(5)	Ti(2)	Cl(6)	95.27(14)	C(6)	P(4)	C(71)	102.3(5)
Rh(1)	P(1)	C(3)	116.9(4)	C(6)	P(4)	C(81)	106.1(5)
Rh(1)	P(1)	C(11)	119.0(4)	C(71)	P(4)	C(81)	106.0(5)
Rh(1)	P(1)	C(21)	109.4(4)	Rh(1)	C(1)	O(1)	179.6(11)
C(3)	P(1)	C(11)	102.6(5)	Rh(2)	C(2)	O(2)	175.4(11)
C(3)	P(1)	C(21)	101.3(5)	P(1)	C(3)	C(90)	114.8(8)
C(11)	P(1)	C(21)	105.7(5)	P(2)	C(4)	C(100)	111.1(7)
Rh(1)	P(2)	C(4)	119.4(4)	P(3)	C(5)	C(95)	109.2(7)
Rh(1)	P(2)	C(31)	104.2(4)	P(4)	C(6)	C(105)	111.9(7)

Table 4.8 (cont.)

Atom1	Atom2	Atom3	Angle
P(1)	C(11)	C(12)	119.1(9)
P(1)	C(11)	C(16)	121.8(10)
P(1)	C(21)	C(22)	122.1(9)
P(1)	C(21)	C(26)	119.0(10)
P(2)	C(31)	C(32)	117.8(9)
P(2)	C(31)	C(36)	124.5(9)
P(2)	C(41)	C(42)	121.1(9)
P(2)	C(41)	C(46)	121.8(10)
P(3)	C(51)	C(52)	120.1(10)
P(3)	C(51)	C(56)	120.5(11)
P(3)	C(61)	C(62)	119.8(11)
P(3)	C(61)	C(66)	119.6(9)
P(4)	C(71)	C(72)	123.2(10)
P(4)	C(71)	C(76)	116.7(9)
P(4)	C(81)	C(82)	121.9(10)
P(4)	C(81)	C(86)	120.9(10)
C(3)	C(90)	C(91)	126.8(11)
C(3)	C(90)	C(94)	127.2(10)
C(91)	C(90)	C(94)	106.1(10)
C(90)	C(91)	C(92)	108.5(12)
C(91)	C(92)	C(93)	108.9(12)
C(92)	C(93)	C(94)	107.6(12)
C(90)	C(94)	C(93)	108.7(12)
C(5)	C(95)	C(96)	126.4(12)
C(5)	C(95)	C(99)	125.3(11)
C(96)	C(95)	C(99)	108.3(11)
C(95)	C(96)	C(97)	108.3(13)
C(96)	C(97)	C(98)	107.4(12)
C(97)	C(98)	C(99)	107.7(11)
C(95)	C(99)	C(98)	107.9(13)
C(4)	C(100)	C(101)	125.6(10)
C(4)	C(100)	C(104)	126.7(11)
C(101)	C(100)	C(104)	107.8(11)
C(100)	C(101)	C(102)	107.7(12)
C(101)	C(102)	C(103)	108.8(12)
C(102)	C(103)	C(104)	106.4(12)
C(100)	C(104)	C(103)	109.2(13)
C(6)	C(105)	C(106)	126.0(11)
C(6)	C(105)	C(109)	124.3(11)
C(106)	C(105)	C(109)	109.5(11)
C(105)	C(106)	C(107)	106.8(12)
C(106)	C(107)	C(108)	109.6(12)
C(107)	C(108)	C(109)	106.3(11)
C(105)	C(109)	C(108)	107.7(12)

each Cp ring is pointing into the center of the cavity. A short separation between the Cp rings on adjacent titanium atoms (for example the H(94)-H(104) distance of 2.76 Å) results in a crowded cavity, as was found for compound **32**, and is depicted in the space filling diagram shown in Figure 4.3.1. Nonetheless, there appears again to be access to the rhodium centers. The reason for the differing orientations of the $Cp^x{}_2TiCl_2$ units in compounds **32** and **34** is not completely clear, although it does seem clear that the stacked Cp arrangement found in **32** does not seem possible for **34**, owing to too small a separation between the Rh ends of the molecule. As was observed for compound **32**, the Ti is bound in a pseudotetrahedral environment, with no significant differences in bond lengths and angles from those found in Cp'_2TiCl_2. See Table 4.6 for a comparison of these values. As in [*cis*-(μ-η^5-$C_5H_4CH_2CH_2PPh_2)_2TiCl_2Mo(CO)_4$] (**30**), the chloride ligands are exposed on the outside of the tetranuclear framework, as shown in Figure 4.3.1. This drawing also indicates that the Cp and phosphorus-bound phenyl groups block the central part of the cavity while still allowing access to at least one of the rhodium centers from within the macrocycle. Figure 4.3.2, an alternate view of compound **34**, in which only the ipso carbon of each phenyl ring is shown, gives a better indication of the relative orientation of the two Rh coordination planes, which are clearly close to parallel, with an angle of 2.3° between the $P_2RhCl(CO)$ least-squares planes. In addition, this drawing, while confirming the steric crowding at both rhodium centers on the inside of the macrocycle, indicates that the coordination sites on the outside of the macrocycle are accessible (approach to Rh(1) is available from the bottom of the diagram or to Rh(2) from the top of the diagram). With the phenyl ring orientation shown in Figures 4.3 and 4.3.1, access to these sites currently is blocked by phenyl rings 2 and 8, but rotation of these groups such that they parallel rings 3 and 5, respectively, should allow for substrate approach to the rhodium centers. The geometry about rhodium is square

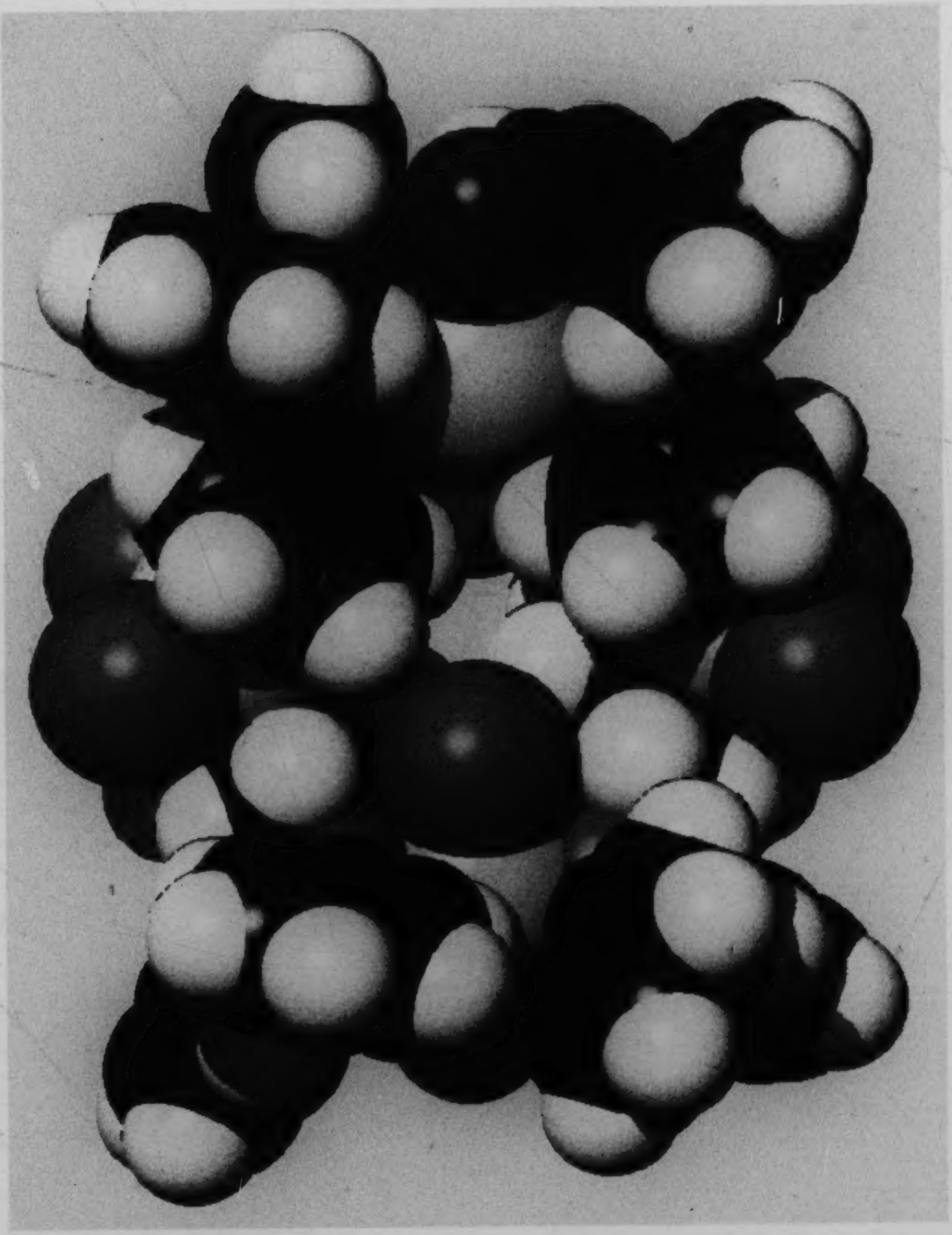


Figure 4.3.1. Space filling depiction of $[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4CH_2PPh_2)_2TiCl_2RhCl(CO)]_2$ (**34**). The orientation is the same as that of Figure 4.3.

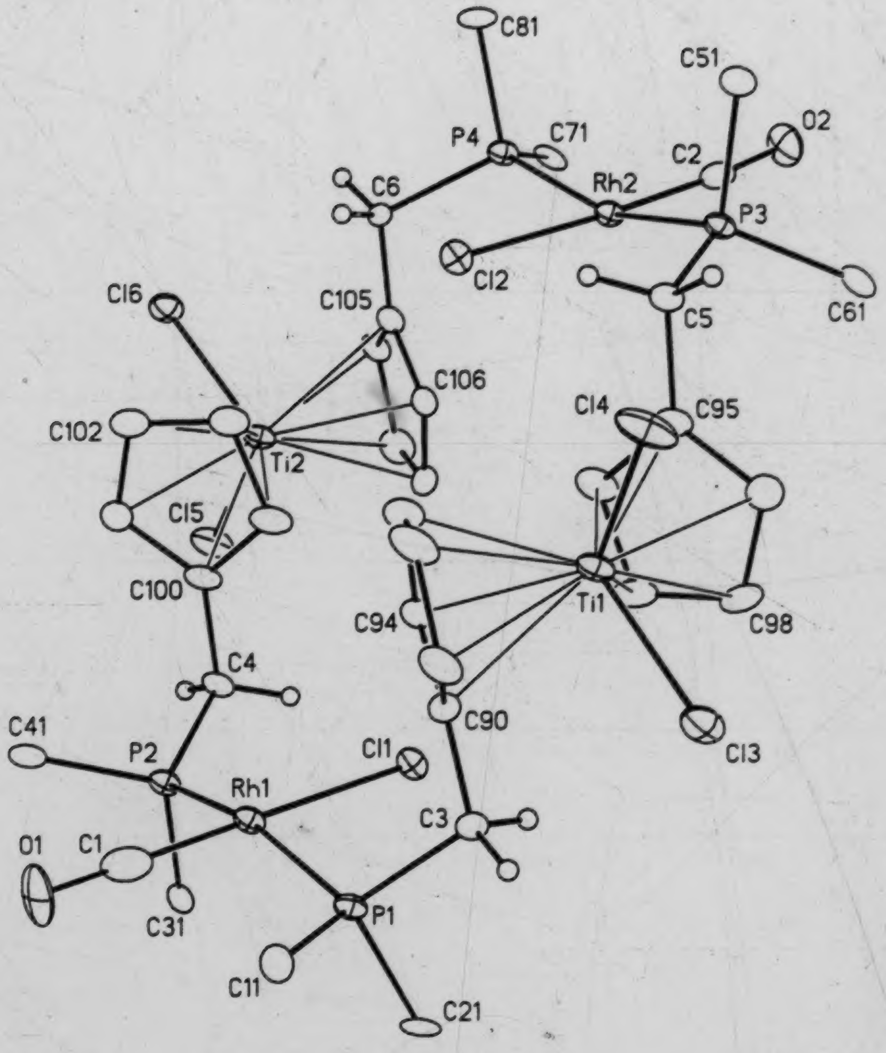

C81
C51
O2
P4
C71
C2
C6
Rh2
P3
Cl2
C5
Cl6
C105
C61
C106
Cl4
C95
C102
Ti2
Cl5
C100
Ti1
C94
C98
C4
C90
C41
P2
Cl1
Cl3
Rh1
C3
O1
C1
C31
P1
C11
C21

Figure 4.3.2 Alternate view of compound **34** showing the relative orientation of the $P_2RhCl(CO)$ planes.

planar, with normal Rh-P bond lengths of *ca.* 2.31 Å. A significant difference in the structure about rhodium between this compound and the previously described compound **32** with a two carbon spacer, is that the P-Rh-P bond angles are quite distorted from the expected 180°, with an average value of 163.5°. As a result the two Rh atoms lie 0.16 and 0.20 Å from their respective coordination planes, being thrust slightly into the cavity. The P(1)-P(3) and P(2)-P(4) separations of 9.455 Å and 9.440 Å, respectively, are longer than the Rh-Rh separation and in the absence of unusual contacts, this may be a result of packing forces. The average Rh-Cl and Rh-CO bond lengths of 2.387(average) Å and 1.76(average) Å and the average Cl-Rh-CO bond angle of 178.0° are similar to those found in compound **32** and in *trans*-$[Rh_2Cl_2(CO)_2(dppm)_2]$. The compound $[(\mu\text{-}\eta^5\text{-}C_5H_4CH_2PPh_2)_2ZrCl_2RhCl(CO)]_2$ (**35**) was prepared similarily and has similar spectroscopic features which will not be discussed here.

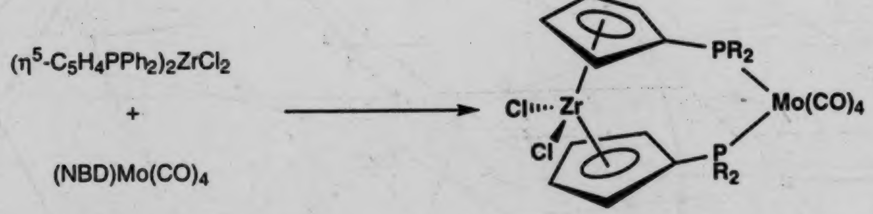
Results obtained in another group suggested it might be possible to prepare early-late binuclear complexes if palladium was used as the late metal.[8e] Accordingly, the reaction of $[(\eta^5\text{-}C_5H_4CH_2PPh_2)_2TiCl_2]$ (**27**) with $(COD)PdCl_2$ was carried out. A single compound $[(\mu\text{-}\eta^5\text{-}C_5H_4CH_2PPh_2)_2TiCl_2PdCl_2]_2$ (**36**) was obtained, the $^{31}P\{^1H\}$ NMR spectrum of which showed a singlet at 22.5 ppm. The ^1H NMR spectrum of **36** showed a AA'BB' signal centered at 6.48 ppm for the cyclopentadienyl hydrogens and a pseudotriplet at 3.80 ppm ($^2J_{PH} = {}^4J_{PH} = 3.3$ Hz) for the methylene-spacer hydrogens. Molecular weight measurements on this compound showed that it is also dimeric in nature, containing a Pd_2Ti_2 core, presumably with a structure analogous to that of $[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4CH_2PPh_2)_2TiCl_2RhCl(CO)]_2$ (**34**).

Discussion

A variety of methods are available for the preparation of early-late heterobimetallic (ELHB) complexes, including halide metathesis reactions with metallocenedihalides and late-metal containing anions, an example of which is shown in equation (1),[21] redox reactions in which a reduced early-metal species reductively cleaves a late metal-metal bond as in equation (2),[22] or by reaction of an early-metal monomer, containing polydentate-ancilliary ligands, with a late-metal source containing labile functionalities, as shown in equation (3).[8a-j, 23]

$$Cp_2ZrI_2 + 2\ K[CpRu(CO)_2] \longrightarrow Cp_2Zr(Ru(CO)_2Cp)_2 \tag{1}$$

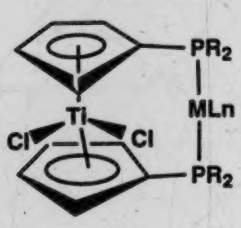
$$Cp'_2V + Co_2(CO)_8 \longrightarrow Cp'_2VCo(CO)_4 \tag{2}$$



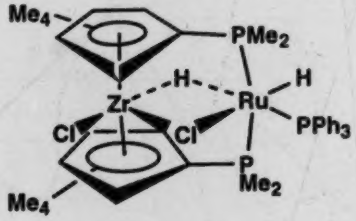
(3)

Although we attempted a variety of methods to prepare ELHB complexes of the type reported in this chapter, we found the most favourable results were obtained with a route similar to that shown in equation (3).

Given that the distance between cyclopentadienyl centroids in a bis-metallocene dichloride complex is typically between 3.8 and 4.0 Å, and the distance between phosphorus nuclei in a trans arrangement on a late metal such as rhodium is about 4.4 Å, the P-Cp axes in these cyclopentadienyl phosphines should be close to parallel in a complex like that shown in **C** below. This means that the substituents on the early metal will be side on with respect to the metal-metal vector in order for a metallocene dichloride to achieve its normal tilt angle of *ca.* 130°. Two representative examples are useful to illustrate this; in the complex $[(\mu\text{-}\eta^5{:}\eta^1\text{-}C_5H_4PPh_2)_2ZrCl_2Mo(CO)_4]$, shown in equation (3) above, in which the phosphines are bound cis to molybdenum, the P-P separation is 3.717 Å, while the Cp(c)-Cp(c) separation is 4.027 Å.[8g] In the complex shown in **D**,[8f] the cyclopentadienyl-bound PMe_2 groups are approximately trans on ruthenium, with a zirconium-derived halide ligand bridging the two metal centers. This orientation results in significant distortion of the $Me_2P\text{-}Ru\text{-}PMe_2$ bond angle from the idealized value of 180° to *ca.* 157°, indicating significant strain in the system. We felt that placing an alkyl spacer between the cyclopentadienyl and phosphine functionalities might alleviate these restrictions by incorporating some flexibility into the Cp-phosphine framework, allowing the early-metal substituents to be directed towards the late metal. This orientation should allow for the study of substituent transfer between the two metal centers, an important aspect of metal-metal cooperativity.



C



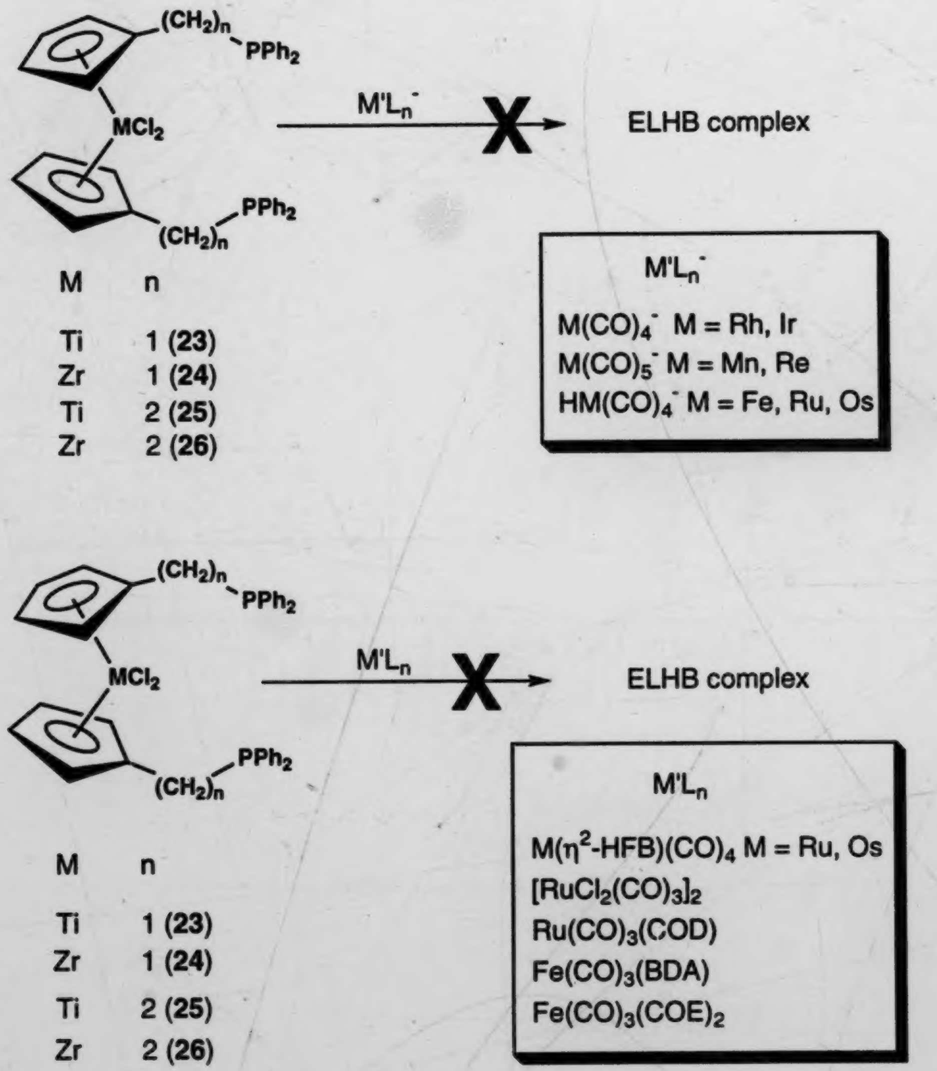
D

Initial attempts at the preparation of ELHB complexes involved the reaction of $[(\eta^5\text{-}C_5H_4(CH_2)_nPPh_2)_2MCl_2]$ (M = Ti (**25**), Zr (**26**) and n = 2; Ti (**27**), Zr (**28**) and n = 1) with late-metal-containing anions. These reactions resulted, in the case of the compounds where M= Ti, in the formation of a number of compounds, and in small amounts of reduction of Ti(IV) to Ti(III), as was indicated by a color change from red to green and by the observation of broadened $^{31}P\{^1H\}$ NMR signals. In the case of the compounds in which M = Zr, the addition of late-metal containing anions resulted in either no reaction or the formation of a multitude of products upon warming. The different combinations attempted are summarized below in Scheme 4.4. These results correspond well with our observation that halide metathesis reactions on these metallocene dichlorides with a variety of alkoxides, which were of interest in that an early-metal-bound alkoxide would provide the possibility of another bridging ligand which may aid in the formation of binuclear ELHB complexes, resulted in the formation of mixtures of mono- and di-alkoxy complexes. This result is likely due to the bulky phenyl substituents blocking access to the metal center.

The attempted reaction of substituted metallocene dichlorides with a variety of group 8 metal sources containing labile functionalities, summarized in Scheme 4.4, also failed to yield isolable ELHB complexes. These reactions produced a multitude of products or no reaction at all, under a variety of conditions.

The first heterobinuclear complexes obtained in our group were $[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)_2TiCl_2Mo(CO)_4]$ (M = Ti (**30**), Zr (**31**)), via the reaction of $[(COD)Mo(CO)_4]$ with $[(\eta^5\text{-}C_5H_4CH_2CH_2PPh_2)_2MCl_2]$ (M = Ti (**25**), Zr (**26**)). Spectroscopic data indicated that the phosphines on molybdenum were mutually cis, and this was confirmed crystallographically. The crystal structures of compounds **30** and **31** showed that the early-metal substituents are not directed towards the molybdenum center, and the metals are quite far apart, at 6.895 Å for compound **30** and 6.945 Å for compound **31**, which is certainly not ideal for metal-metal cooperativity. The similarity of the spectroscopic and crystallographic data for compounds **30** and **31** suggest that the compounds consists of relatively unperturbed $P_2Mo(CO)_4$ and $(\eta^5\text{-}C_5H_4R)_2MCl_2$ units. These results are similar to those obtained in another group, from the reaction of $[(\eta^5\text{-}C_5H_4PPh_2)ZrCl_2]$ with

Scheme 4.4


(CH2)n
PPh2
MCl2
PPh2
(CH2)n
M'Ln-
ELHB complex
(CH2)n
PPh2
MCl2
PPh2
(CH2)n
M'Ln
ELHB complex

M	n
Ti	1 (**23**)
Zr	1 (**24**)
Ti	2 (**25**)
Zr	2 (**26**)

$M'L_n^-$

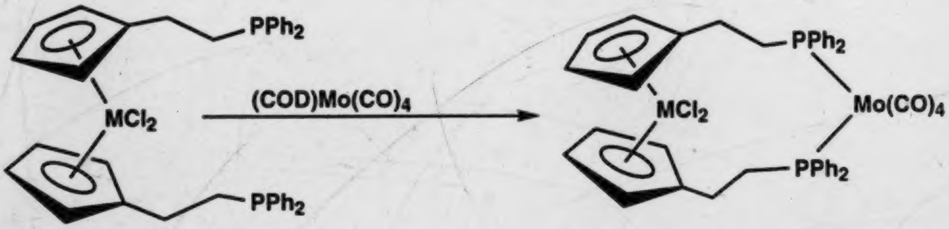
$M(CO)_4^-$ M = Rh, Ir
$M(CO)_5^-$ M = Mn, Re
$HM(CO)_4^-$ M = Fe, Ru, Os

M	n
Ti	1 (**23**)
Zr	1 (**24**)
Ti	2 (**25**)
Zr	2 (**26**)

$M'L_n$

$M(\eta^2\text{-HFB})(CO)_4$ M = Ru, Os
$[RuCl_2(CO)_3]_2$
$Ru(CO)_3(COD)$
$Fe(CO)_3(BDA)$
$Fe(CO)_3(COE)_2$

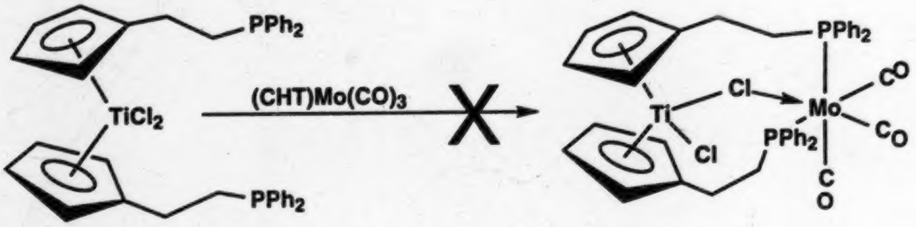
(NBD)Mo(CO)$_4$ (NBD = norbornadiene). The crystal structure of the product, [(μ-η^5:η^1-C$_5$H$_4$PPh$_2$)$_2$ZrCl$_2$Mo(CO)$_4$] again showed that the phosphine groups were bound cis on molybdenum, as is expected based on the Cp(centroid)-Cp(centroid) and P-P separations discussed previously, and that the halides on zirconium were directed away from the molybdenum center.[8g] The structure of this compound is similar in many respects to that of compound **31**, except for the larger metal-metal separation and the larger P-M-P angle of 100.87(8)° in compound **31**, with the latter resulting in compression of the C(1)-P-C(4) angle to 83.3(4)° from the ideal 90° for the carbonyl ligands trans to the phosphine groups. The larger P-M-P angle is likely due to the apparent preference of the phosphinoalkyl arms of the metalloligand [(η^5-C$_5$H$_4$CH$_2$CH$_2$PPh$_2$)$_2$ZrCl$_2$] to be as far apart as possible. The structural similarities between this compound and that of the mononuclear units Cp'$_2$ZrCl$_2$[15] and (dppm)$_2$Mo(CO)$_4$[16] led the authors to suggest that the complex may exhibit the reactivity of the unperturbed mononuclear units.



M = Ti (**25**), Zr (**26**)

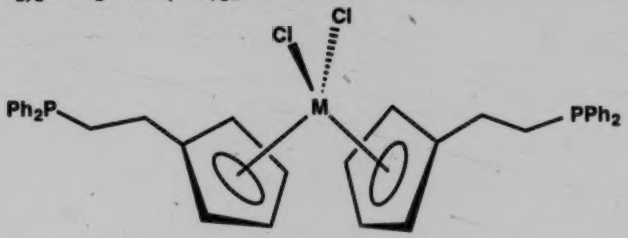
M = Ti (**30**), Zr (**31**)

In order to obtain a complex in which the metals were closer together, the reaction of **25** with (CHT)Mo(CO)$_3$ (CHT = cycloheptatriene) was carried out, in the hope that a halide on titanium would take up the third coordination site on molybdenum from the labile CHT goup. Model building had suggested that the three facial sites on Mo, vacated by the CHT ligand, could be occupied by the two phosphines and a bridging chloride, as is shown below. It was found however, that the reaction produced **30** as the major product, presumably through the scavenging of CO from the many decomposition products evident in the NMR spectrum of the reaction mixture. In addition, heating solutions of compounds **30** and **31** in order to remove a carbonyl or to effect the isomerization to compounds in which the phosphines were in a trans arrangement (as there are no readily available *trans*-Mo(CO)$_4$ sources) were unsuccessful.



25

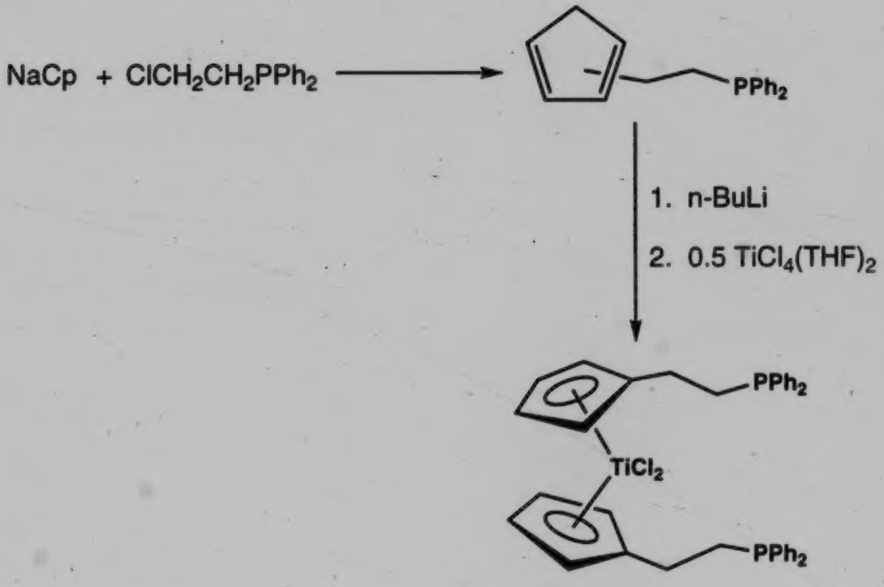
Although we had failed to obtain a heterobimetallic system in which the metals were in close proximity, the preparation of **30** and **31** were nevertheless encouraging in that binuclear products were obtained, so it was decided to investigate the reactivity of the early-metal monomers, $[(\eta^5\text{-}C_5H_4CH_2CH_2PPh_2)_2MCl_2]$ (M = Ti (**25**), Zr (**26**)) with late-metal sources in which phosphines typically bind in a trans arrangement. Accordingly, the reactions of **25** and **26** with a variety of Rh sources were carried out. When solutions of these complexes and $[RhCl(CO)_2]_2$ were mixed under a variety of conditions, the signals in the NMR spectra of the resultant products were broad and unresolved. The most likely explanation for this observation is that mixtures of compounds were forming, with each compound having similar chemical shifts in the $^{31}P\{^1H\}$ and ^1H NMR spectra. The formation of these mixtures is likely a result of the inherent flexibility of the phosphine arms on the cyclopentadienyl rings, which, due to steric interactions, are likely oriented at *ca.* 180 °C from each other in solution, similar to what is observed in the solid state of compound **26** (*vide supra*), and as has been observed in other related substituted zirconocene dichlorides.[8e, 24] The products from the above reactions are likely oligomeric in nature, of the form $[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)_2MCl_2RhCl(CO)]_n$, where M = Ti or Zr. If however, solutions of **25**



M = Ti (**25**), Zr (**26**)

or **26** are added simultaneously along with a solution of $[RhCl(CO)_2]_2$ to cold THF (high dilution conditions), isolable compounds were obtained. It was found that the reaction of **23** with $[RhCl(CO)_2]_2$ under these conditions produced two isomeric compounds, "*α*"-$[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)_2TiCl_2RhCl(CO)]_2$ (**32**) and "*β*"- $[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4\text{-}CH_2CH_2PPh_2)_2TiCl_2RhCl(CO)]_2$ (**33**) in a *ca*. 2:1 ratio. Compound **32** has been reported previously by Poilblanc,[8d] and was obtained from the reaction of $[Rh_2Cl_2(CO)_2(C_2H_4)_2]$ with $[(\eta^5\text{-}C_5H_4CH_2CH_2PPh_2)_2TiCl_2]$ (**25**) where compound **25** was prepared as shown in Scheme 4.5 below. In our hands, the reaction of NaCp with $ClCH_2CH_2PPh_2$, never proceeded efficiently and we were not able to obtain compound **25** pure via this method. Our repeated failures with the procedures outlined certainly casts doubt upon the claim that *α*-$[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)_2TiCl_2RhCl(CO)]_2$ (**32a**) had been obtained as a pure compound. This problem was compounded by the fact that the report of **32** appeared as a preliminary Communication in which no experimental details, or elemental analyses of the products were given. We were also concerned that the characterization of this complex, containing two Ti and two Rh atoms, was based solely on a comparison of

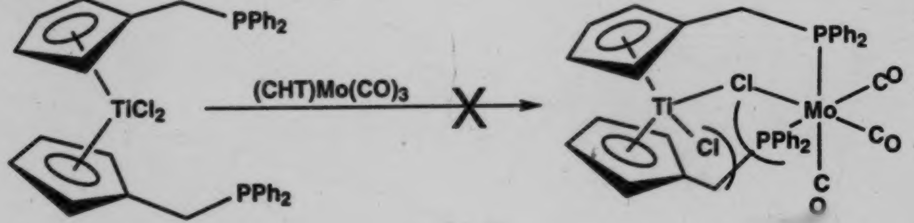
Scheme 4.5


NaCp + ClCH2CH2PPh2
PPh2
1. n-BuLi
2. 0.5 TiCl4(THF)2
PPh2
TiCl2
PPh2

25

the ${}^{31}P\{{}^{1}H\}$ NMR and IR data with that of *trans*-[$Rh_2Cl_2(CO)_2(Ph_2P(CH_2)_nPPh_2)_2$] and we did not see how this assumption was justified. We reasoned that both binuclear and tetranuclear (and in fact, higher nuclearity as well) complexes should have similar ${}^{31}P$ NMR spectra if both had a trans-phosphine, square planar coordination at rhodium. Accordingly, once we had a convenient method for the preparation of pure **25**, we set out to prepare and complete the characterization of compound **32**. Also troubling in the initial report was the fact that in our hands most preparations of compound **32** had yielded mixtures of large numbers of presumably oligomeric products, which as was noted earlier, we believe to be a consequence of the favoured orientation of the alkylphosphino arms bound to the cyclopentadienyl rings. In addition, there was no mention in this Communication of the fact that the tetranuclear complex **32a** isomerizes in solution to form a complex which mass spectral data suggests also contains four metals. We obtained a single crystal from a mixture of compounds **32a** and **32b**, the X-ray structure of which demonstrated unambiguously that $(\eta^5\text{-}C_5H_4CH_2CH_2PPh_2)_2TiCl_2$ was acting as a bridging metalloligand, much like dppm, forming a complex similar to *trans*-[$Rh_2Cl_2(CO)_2(dppm)_2$], in which the bridging dppm ligands are replaced by a bridging $(\eta^5\text{-}C_5H_4CH_2CH_2PPh_2)_2TiCl_2$ unit. The X-ray structure of compound **32** shows that there is little difference in bond lengths and angles about Ti and Rh, when compared to those of the analogous species, Cp'_2TiCl_2 and *trans*-[$Rh_2Cl_2(CO)_2(dppm)_2$]. These data, in conjunction with the large metal-metal separations, suggest that the complex will behave as isolated $(\eta^5\text{-}C_5H_4R)_2TiCl_2$ and $(R_3P)_2RhCl(CO)$ fragments. Further support for this is obtained when the analogous Zr/Rh-containing species, $[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)_2\text{-}ZrCl_2RhCl(CO)]_2$ **33** is considered. This compound has almost identical spectroscopic properties to compound **32a**, which indicates that replacing Ti for Zr has little effect on the structure of the product. This compound also isomerizes slowly to form a new complex, which presumably has a structure similar to the analogous titanium-containing compound **32b**.

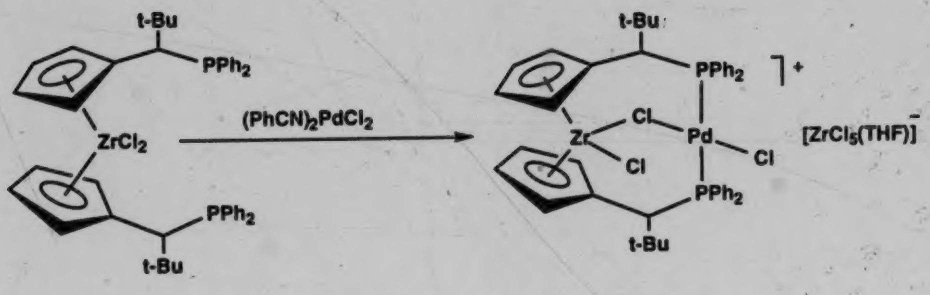
Our lack of success in obtaining heterobinuclear species having a trans-phosphine alignment at the late metal with the $C_5H_4CH_2CH_2PPh_2$ bridging ligand, led us to attempt to generate such species using the shorter-bite ligand $C_5H_4CH_2PPh_2$. This ligand is intermediate between that described above, which is apparently too long, and the $C_5H_4PPh_2$ ligand, which appears to be too short. The early-metal-containing, monomer precursors for this chemistry are $[(\eta^5\text{-}C_5H_4CH_2PPh_2)_2MCl_2]$ (M = Ti (**27**), Zr (**28**)). Initial attempts at the preparation of binuclear complexes involved the reaction of compound **27** with (CHT)Mo(CO)$_3$. This molybdenum source was chosen, based on the results of the reaction of $[\eta^5\text{-}C_5H_4CH_2CH_2PPh_2)_2TiCl_2]$ (**25**) with (COD)Mo(CO)$_4$ in which the product had cis-phosphines. It was hoped that by using a fac-substituted precursor that loss of the labile CHT ligand would yield a product in which two of the facial sites would be occupied by the pendant phosphines, while a titanium-bound halide would take up the third coordination position. This reaction was unsuccessful and produced a multitude of products under a range of conditions. We suggest that the failure was likely due to unfavourable steric interactions between the presumed terminal titanium-bound halide and phosphine groups on molybdenum, as shown below. This result is reminiscent of our failure to obtain an analogous species using the $C_5H_4CH_2\text{-}CH_2PPh_2$ ligand.



27

The reaction of compounds **27** and **28** with $[RhCl(CO)_2]_2$ provided more favourable results, however, giving single compounds $[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4CH_2PPh_2)MCl_2\text{-}RhCl(CO)]_2$ (M = Ti (**34**), Zr (**35**)) under the appropriate conditions. Single crystals of compound **34** were obtained and the X-ray structure showed that, again, a macrocyclic product containing two titanium and two rhodium nuclei had been formed. As was observed for $[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)_2TiCl_2RhCl(CO)]_2$ (**32**), the bond lengths and angles are not significantly different from those in *trans*-$[Rh_2Cl_2(CO)_2(dppm)_2]$[17] and Cp'_2TiCl_2,[14] indicating that the geometry around rhodium and titanium is not significantly perturbed by the presence of another metal. The structures of compounds **32** and **34** are remarkably similar in the sense that both $RhCl(CO)P_2$ planes in each molecule are essentially parallel, and offset from each other in a step-like manner. As expected the additional CH_2 link between the C_5H_4 and PPh_2 groups in compound **32** results in a greater separation between the $RhCl(CO)P_2$ planes than in **36** (ca. 9.58 Å vs. 6.18 Å), and a resulting greater separation (11.88 Å vs. 9.01 Å) between the rhodium centers. The Ti-Ti separation is slightly shorter (7.35 Å vs. 8.25 Å) in compound **32**, having the two-carbon spacer between the Cp and phosphine moieties. Addition of this extra CH_2 unit also results in subtle orientation differences of the Cp'_2TiCl_2 moieties, although in both cases the chloro ligands are on the periphery of the macrocycle, pointing out.

Results obtained from Erker's laboratory suggested that binuclear species might be obtained if palladium was used as the late metal. This group had reported the formation of binuclear Zr/Pd-containing species with bridging ligands very similar to ours, in which the hydrogens on the spacer carbon between the Cp and PR_2 units were substituted by one or more alkyl groups. The assumption that the products obtained with these $C_5H_4\text{-}CH(R)PPh_2$ ligands were all binuclear appears to have been based on the X-ray structure of a product obtained in low yield from the reaction shown below.[8c]



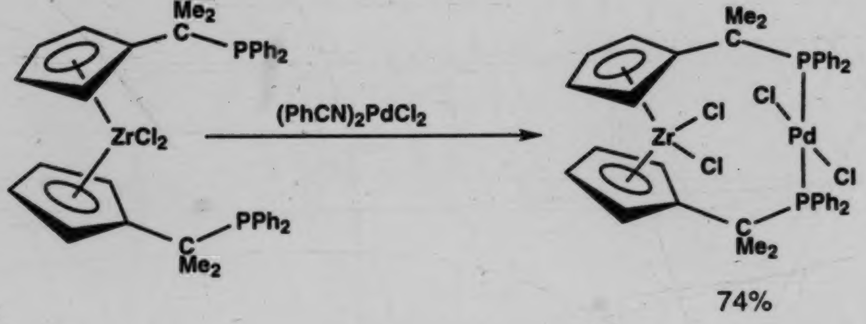
(4)

7 %

J

An analogous reaction carried out by us, between $[\eta^5\text{-}C_5H_4CH_2PPh_2)_2MCl_2]$ **(27)** and $[(COD)PdCl_2]$, has instead yielded $[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4CH_2PPh_2)_2TiCl_2PdCl_2]_2$ **(38)**. As with the analogous Rh/Ti containing species, the molecular weight determinations indicate that a dimeric product, containing two titanium and two palladium atoms was formed. Certainly we had anticipated that substitution of the methylene hydrogens by larger substituents would have an influence on the structure. This would seem to be most obvious for the C_2H_4-linked species, $[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)_2TiCl_2RhCl(CO)]_2$ **(32)**, in which one of every two methylene groups points into the center of the macrocycle, such that adding larger substituents would be expected to destabilize macrocycle. However, the effect of substituting one or both hydrogens on the spacer methylene groups in compound **34**, having only one CH_2 group connecting the Cp and PPh_2 moieties (analogous to the Erker compounds), is not obvious, since these groups are aimed away from the center of the macrocycle. In order to confirm either our suggestion or Erker's proposal, we have attempted to repeat the reaction shown below, as reported by Erker. At this stage our results do not match those reported, where instead of a high yield of the binuclear product **F**, we consistently obtain mixtures of products, the mass spectra of which show the presence of both binuclear and tetranuclear species. Without doubt, this chemistry benefits greatly from "user experience", and we anticipate that after suitable experience with this ligand system we will be able to duplicate the results of

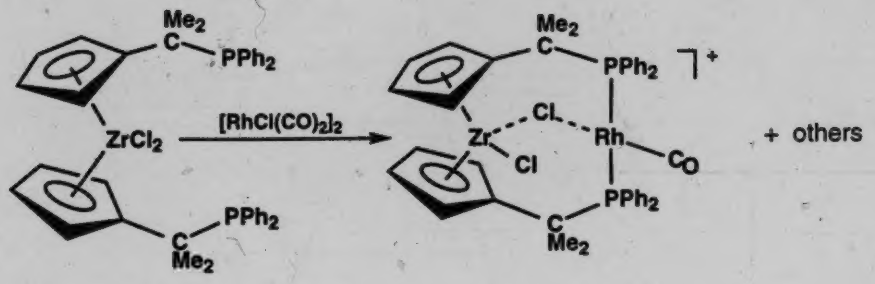
Erker. Nevertheless, the observation of significant amounts of binuclear product is encouraging.



(5)

E **F**

We have also carried out reaction of the substituted zirconocene dichloride shown in **E** above[8c] with rhodium sources, in the hope that IR spectroscopy would provide a clue as to the nature of the products obtained. It seemed likely that products similar to those formed in the reaction shown in equation (4) would be produced when replacing Pd(II) with the larger Rh(I), since the neutral binuclear complex in **F** already appears to be quite crowded in the $ZrCl_2PdCl_2$ plane. If this is the case and a binuclear complex is formed, then the "Pd-Cl" fragment should be replaced with a "Rh-CO" unit. The result of this reaction was a complex mixture of products. An IR spectrum of the mixture, however, only showed CO bands at 2065 cm^{-1} and 1975 cm^{-1} with the lower frequency band being of much higher intensity. If our assumption that the higher frequency band belongs to a cationic binuclear complex and the band at 1975 cm^{-1} corresponds to neutral oligomeric species, then this reaction appears to parallel the reaction shown in equation (4) above in which the cationic binuclear complex was obtained in low yield. This would support our suggestion that the majority of the species obtained are oligomeric. At the very least, the results of the reaction shown in equation (4) are encouraging in that they

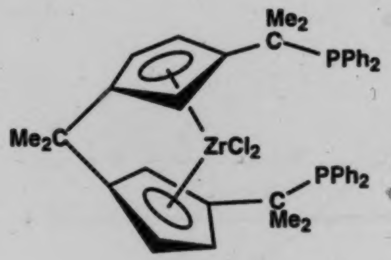


E

(6)

show that binuclear complexes may be obtained with metallocene dichlorides containing $C_5H_4CR_2PPh_2$ ligands.

The results above suggested that restricting the rotational freedom of the alkylphosphine groups by the inclusion of alkyl moieties on the C_1 spacer would not by itself be sufficient to result in the formation of binuclear species being favoured over oligomeric products. Consequently we prepared the *ansa*-metallocene dichloride shown below, in which both the rotational flexibility of the alkylphosphino groups and of the cyclopentadienyl rings was presumably reduced. We felt that the dimethylmethyl linker in complex **29** would reduce the ability of the Cp rings to rotate the alkylphosphino arms away from each other, and instead, keep them in a close-to-eclipsed arrangement. In addition, as shown in Figure 4.3, in which the $Cp^x{}_2TiCl_2$ moieties come into close contact at the center of the macrocycle, a Me_2C linker would destabilize this contact and may instead favour a binuclear arrangement.



29

The use of a one-carbon linker between the cyclopentadienyl rings should also result in a smaller Cp(c)-Zr-Cp(c) angle,[25a] which could actually increase the rotational flexibility within the alkylphosphino arms relative to that in the non-ansa derivative shown above in E. When compound **29** was reacted with rhodium sources, complex mixtures were obtained, the IR spectra of which showed bands at ca. 2060 cm^{-1} and 1970 cm^{-1}, which we believe are due to binuclear and oligomeric products, respectively, as was discussed previously. When compound **29** was reacted with $(PhCN)_2PdCl_2$ under the same conditions used by Erker *et al* in the reaction shown above in equation (5), the ^{31}P NMR spectra of the resultant products showed the presence of more compounds than we had found when the non-linked species were used. If the Me_2C linker is replaced with a Me_2Si unit, then the Cp(c)-M-Cp(c) angle will be similar to the non-ansa-metallocene dichlorides[25b] and certainly this approach is worth pursuing as in this system, there should be decreased conformational flexibility within the alkylphosphino arms relative to that of **29**. In addition, macrocycle formation should be disfavoured for the reasons mentioned above.

Although the number of ligands used in this study is small, the results above suggest that the formation of tetranuclear and higher nuclearity complexes is governed more by the orientation of the alkylphosphino arms than by that of the cyclopentadienyl rings. It appears that a Cp-alkylphosphine containing a two-carbon spacer between the Cp and PR_2 moieties is too long to allow for M-M cooperativity in ELHB complexes bridged by this type of ligand system. Ligands with a one-carbon spacer appear to be more appropriate for the preparation of ELHB complexes, and certainly these results warrant a systematic study of the product distribution in the reactions of ansa and non-ansa alkylphosphino-substituted metallocene dichlorides with late-metal sources.

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Chapter 5
Conclusions

The objectives of this thesis were to develop the organometallic chemistry of multinuclear systems containing late- and mid-metals (rhodium-group 6 combinations) and that of systems containing both early- and late-transition metals. It was hoped that these studies would result in an increased understanding of the roles of an adjacent metal in the reactivity of the system. Our interest in this phenomenon stems from the possible importance of metal-metal cooperativity between metals on the surface of a heterogeneous catalyst, or in a homogeneous catalyst containing more than one metal.

In the Rh/group 6 system, several hydrocarbyl complexes were prepared, of the general form $[RhM(R)(CO)_4(dppm)_2]$ (M = Mo, R = CH_3, vinyl, allyl, phenyl, acyl, benzyl; M = W, R = vinyl), either by halide metathesis on $[RhM(CO)_4(\mu\text{-}Cl)(dppm)_2]$ (M = Mo (**2**), W (**3**)) or by alkyne insertion reactions with $[RhMo(CO)_4(\mu\text{-}H)(dppm)_2]$ (**1**). In all cases, the hydrocarbyl moiety was η^1-bound to the 16 electron, square-planar rhodium center, independent of whether this group was an alkyl, vinyl, allyl, acyl or aryl. Based on the spectroscopic properties of these compounds, it is clear that their structures are very similar.

In the hydrocarbyl species prepared in this study, bridging carbonyl bands were a feature found in the IR spectra of all products. Rhodium coupling was not observable in the $^{13}C\{^1H\}$ NMR spectra of many of the species, so the magnitude of the bridging interaction could not be determined. Some of the compounds did display Rh-CO coupling, though, and in these cases the coupling constants indicated the interaction was of a weak semibridging nature. This semibridging interaction serves to remove excess electron density from the rhodium center, due to the lack of any π-acidic ligands on this metal, as well as the presence of two donor phosphine groups and a dative Mo→Rh bond. We had anticipated that the coupling of the semibridging CO to rhodium in the $^{13}C\{^{1}H\}$ NMR spectra could be correlated with the basicity of the hydrocarbyl unit, but the breadth of the resonances precluded measuring many of these coupling constants. It was expected, as has been observed in other systems studied in our group,[1a] that the interaction would be stronger in the complexes with good σ-donor alkyl groups such as $[RhMo(CH_3)(CO)_4(dppm)_2]$ (**10**) than in those with electron-withdrawing groups such as $[RhMo(C(CF_3)=CH(CF_3))(CO)_4(dppm)_2]$ (**5**) and $[RhMo(C(CO_2Me)=CH(CO_2Me)-(CO)_4(dppm)_2]$ (**4**).

A ligand arrangement in which the hydrocarbyl fragment is bound to the rhodium center has parallels to several other systems prepared in our group, including Rh/Mn,[2] Rh/Re,[3] Rh/Os,[1] and Rh/Ru.[4] The Rh/Ir system, however provides an exception to this in that the alkyl group in $[RhIr(CH_3)(CO)_n(dppm)_2][OTf]$ has the methyl group bound to the 18e iridium center,[5] although the addition of ligands such as ethylene (n=3)[5] or iodide (n=2)[6] results in methyl migration to the rhodium center. Clearly, there are subtle factors involved in dictating whether the alkyl group is bound to one metal or the other which are not clearly understood, and these are certainly of interest if the role of the different metals in the reactivity of such fragments is to be determined. One undoubtedly important factor involved in the hydrocarbyl fragment location in the Rh/M (M = Mo, W) system relates to the resulting oxidation states involved. In this system, as well as in the others, having the hydrocarbyl fragment on rhodium results in a favoured Rh(I)/M(0) oxidation-state assignment, whereas having the hydrocarbyl group on the other earlier metal gives rise to a less favourable Rh(0)/M(I) formulation.

We had hoped to study the reactivity of these hydrocarbyl-containing complexes with electrophiles, such as protic acids and methyl triflate in order to examine a variety of reaction types, such as migratory insertions and reductive eliminations. For the most part, however, this system proved to be quite unreactive, in contrast to the analogous Rh/Os system.[1] Although the Rh/Os system, like the present Rh/Mo complexes, has coordinative unsaturation at rhodium, and was saturated at the other metal, an important difference seems to be the coordination about the saturated metal. Whereas osmium is five coordinate, the molybdenum center in analogous compounds is six coordinate. This added crowding in the latter class seems to prevent the addition of electrophiles, which occurs readily in the Rh/Os system, forming cationic species which are isoelectronic with the neutral Rh/Mo hydrocarbyl species prepared in this study. It is significant, that in the previously studied Rh/Os system, electrophilic attack occurs at the saturated osmium center. The effect of having Mo *vs*. Os in the system can be illustrated in the reactions of the methyl species $[RhM(CH_3)(CO)_n(dppm)_2]$ (M = Mo, n = 4; M = Os, n = 3) with protic acids. While the Rh/Os complex readily adds a proton at osmium at -80°C,[1a] the analogous Rh/Mo species does not react with this reagent until *ca.* 10°C. One notable exception to this lack of reactivity, however, is the reaction of the vinyl species, $[RhMo(CH{=}CH_2)(CO)_4(dppm)_2]$ (**8**) with HBF_4. In this case, reaction occurs at -80°C to form the cationic alkylidene-containing species, $[RhMo({=}CH(CH_3))(CO)_4(dppm)_2][BF_4]$ (**15**), which subsequently rearranges to the ethylene adduct, $[RhMo(\eta^2\text{-}C_2H_4)(CO)_4(dppm)_2][BF_4]$ upon warming. The large temperature difference for the occurrence of this reaction between the vinyl species **15** and that of the methyl complex **10** suggests that the proton directly attacks the π-bond of the vinyl moiety, rather than at either metal center, whereas electrophilic attack in compound **10** likely occurs at the square-planar rhodium center. This suggests that the steric congestion at the molybdenum center plays a role in decreasing the reactivity of the complex at rhodium also.

Another interesting reaction performed in this study is that of $[RhMo(CO)_5(dppm)_2][PF_6]$ with CH_2N_2. It had been observed previously in our group that $[RhOs(CO)_4(dppm)_2][BF_4]$ reacts with this reagent at ambient temperature to form the allyl-methyl containing species $[RhOs(\eta^1\text{-}C_3H_5)(CH_3)(CO)_4(dppm)_2][BF_4]$.[1b] Since this transformation has direct relevance to the Fischer-Tropsch reaction, it was of interest to determine the effect of exchanging Os for Mo. Although the addition of excess CH_2N_2 to $[RhMo(CO)_5(dppm)_2][PF_6]$ did produce a small amount of a new species, with characteristic vinyl resonances in the ^1H NMR spectrum, isolation of the new complex proved to be impossible due to the large amount of the starting material present in the reaction mixture. Certainly, further studies on this system, with the heavier congeners Ir or W, are warranted, as an expected stronger third-row metal-carbon bond may allow for the isolation of a species containing diazomethane-derived organic fragments.

The second goal of this thesis was to develop the chemistry of a series of metallocene dichlorides of the form $[(\eta^5\text{-}C_5H_4(CR_2)_nPPh_2)_2MCl_2]$, where M = Ti or Zr and n = 1, or 2, with a variety of late metal sources for the formation of ELHB complexes. As this reactivity in complexes where n = 0 has been reasonably well studied, comparison of the results obtained in the former systems was of interest to see if any correlation between the types of ELHB complexes obtained and the geometric attributes of the bridging ligand could be obtained.

Although the earlier literature in this area had made it appear that entry into the $C_5H_4CH_2CH_2PPh_2$ system should be straightforward,[7] this proved not to be the case, and these reported routes were abandoned in favour of a later report on this ligand. Once an appropriate synthetic method had been found for this ligand, the metallocene dichloride derivatives, $[(\eta^5\text{-}C_5H_4CH_2CH_2PPh_2)_2MCl_2]$ (M = Ti (**25**), Zr (**26**)) were prepared, and compound **26** was characterized crystallographically. The X-ray structure showed that the complex is well set up for either the formation of binuclear or multinuclear species, and both types of complexes were obtained. The binuclear complexes $[(\mu\text{-}\eta^5:\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)_2MCl_2Mo(CO)_4]$ (M = Ti (**30**), Zr (**31**)) were obtained, and both characterized by single crystal X-ray techniques, which showed few differences between them. The only significant difference between these structures and that of the previously characterized $[(\mu\text{-}\eta^5:\eta^1\text{-}C_5H_4PPh_2)_2ZrCl_2Mo(CO)_4]$[8] was the longer Zr-Mo distance, which was expected based on the longer separation between the C_5H_4 and PPh_2 moieties, and the distorted *cis*-P-Mo-P bond angle. The large P-Mo-P angle seems to indicate that the alkylphosphino arms of the metalloligand prefer to be as far apart as possible. Switching to a late metal system that favours a mutually trans arrangement of the phosphine arms, we have succeeded in synthesizing the early-late heteronuclear complexes $[(\mu\text{-}\eta^5:\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)_2MCl_2RhCl(CO)]_2$ (M = Ti (**32a** and **b**), Zr (**33a** and **b**)). However, these complexes are not the targeted binuclear species, but contain four metals. These compounds all have rather large metal-metal separations, ranging from ca. 6.9 Å to 11.9 Å, and likely will not be useful for metal-metal cooperativity studies. The preference for the alkylphosphino arms to be far apart may be due to steric interaction of the bulky diphenylphosphino groups, and if so, it would be of interest to prepare the dimethylphosphino analogues in which this effect should be substantially lessened. It is interesting to note the highly specific conditions required for the formation of the Rh/Ti and Rh/Zr species **32** and **33**, i.e. high dilution and low temperature. The observation that large numbers of oligomeric compounds are formed under other conditions suggests that this result is due to the presumably high rotational flexibility of the $CH_2CH_2PPh_2$ arms. When the spacer length is decreased, as in the compounds $[(\eta^5\text{-}C_5H_4CH_2PPh_2)_2MCl_2]$ (M = Ti (**27**), Zr (**28**)), then isolable heteronuclear compounds are easily obtained in the reactions of these mononuclear species with late-metal sources.

The products from the reactions of compounds **27** and **28** with both $[RhCl(CO)_2]_2$ and $(COD)PdCl_2$, , were the tetranuclear species, $[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4CH_2PPh_2)_2MCl_2RhCl(CO)]_2$ (M = Ti (**34**), Zr (**35**)) and $[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4CH_2PPh_2)_2TiCl_2RhCl(CO)]_2$ (**36**). The ease of formation of these complexes relative to compounds **32** and **33** suggests that fewer conformations are available in the alkylphosphino arms in the metalloligands **27** and **28**, compared to the analogues with two carbon spacers, compounds **25** and **26**. Alternatively, higher oligomers may be disfavoured in the C_1 system, for reasons that are not clear.

One way to decrease the flexibility within the metalloligand system is to use an ansa-metallocene dichloride derivative. Connecting the Cp rings with a Me_2C linker group should have two effects. The first is to restrict the ability of the phosphine arms to rotate away from each other, and the second effect, depending on the linker chosen, is to change the Cp(c)-M-Cp(c) angle. For the Me_2C linker, this will result in a decrease of this angle, and accordingly, the phosphine arms should have more rotational flexibility about the C_5H_4-alkyl bond relative to a non-ansa analogue. Preliminary studies on the reactions of our *ansa*-$[Me_2C(C_5H_3CMe_2PPh_2)_2ZrCl_2]$ (**29**) with palladium sources gave more complex mixtures than that of the non-ansa complex, $[(\eta^5\text{-}C_5H_4CMe_2PPh_2)_2ZrCl_2]$.[9] It therefore appears that the formation of oligomeric species is governed more by the flexibility of the phosphine arms than by the rotational freedom of the Cp groups. To provide further support for this effect, the Me_2Si linked ansa-metallocene derivative should be prepared, as this species should have a Cp(c)-M-Cp(c) angle similar to the non-ansa analogue, due to the larger size of silicon compared to carbon.[10] Another approach that merits further study is related to the Erker study[9] in which the binuclear complex, $[(\eta^5\text{-}C_5H_4CH(^tBu)PPh_2)_2ZrCl_2]$, was obtained in low yield. In this compound, the spacer carbon is substituted with a very bulky t-Bu group, which one would expect to significantly decrease, if not lock the conformational freedom of the alkyl phosphino arms. The effect of this decrease in conformational flexibility in not obvious, and certainly deserves more study.

These results seem to indicate that a systematic study of linker-carbon substitution patterns *vs.* product distribution in the reactions of metallocene dichlorides substituted with alkylphosphino groups with rhodium sources is warranted. It would also be interesting to correlate these findings with the solid-state orientation of the phosphino arms, as this may lead to ligand systems suitable for the preparation of binuclear Rh/Ti-containing complexes with which metal-metal cooperativity could be studied. Based on our failure in preliminary studies to duplicate Erker's findings, it is clear that the conditions needed to obtain heterobinuclear complexes need further study. As we had noted the formation of cationic, presumably binuclear species in the reactions of our metallocene dichlorides with rhodium sources, it of interest to vary the solvent system, in that a more polar solvent may induce halide loss and aid in the formation of a halide-bridged ELHB complex, like that obtained by Erker. Similarly, the addition of halide abstractors, such as Ag^+, in promoting the formation of the presumed cationic, halide-bridged binuclear product should be tested.

The catalytic relevance of metal-bound hydrocarbyl species prompted us to attempt alkylation reactions on these early-late heteronuclear complexes. However, since we were not able to successfully alkylate the preformed heteronuclear complexes, it is of interest to prepare hydrocarbyl-containing, early-metal monomers. These complexes could be used for reaction with late metal sources as an alternative route to ELHB hydrocarbyl complexes. If the early-metal-bound hydrocarbyl fragments are unsaturated, such as an alkynyl group, then the C≡C bond may also provide an extra bridging interaction with the late metal which could aid in the formation of binuclear products.

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